PB82-231853

Proceedings: EPA's Industry Briefing on the Adipic Acid Enhanced Limestone FGD Process (July 1981)

(U.S.) Industrial Environmental Research Lab.
Research Triangle Park, NC

Jun 82

U.S. Department of Commerce
National Technical Information Service
NTIS

United States
Environmental Protection
Agency

EPA-600/9-82-012
June 1982

EPA

Research and Development

PB82-231853

PROCEEDINGS: EPA'S
INDUSTRY BRIEFING ON THE
ADIPIC ACID ENHANCED
LIMESTONE FGD PROCESS
(July 1981)

Prepared for

Office of Environmental Engineering and Technology

Prepared by

Industrial Environmental Research
Laboratory
Research Triangle Park NC 27711

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.
EPA-600/9-82-012

2.

3. RECIPIENT'S ACCESSION NO.
PB82-231853

4. TITLE AND SUBTITLE
Proceedings: EPA's Industry Briefing on the Adipic Acid Enhanced Limestone FGD Process (July 1981)

5. REPORT DATE
June 1982

6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)
J. David Mobley, Compiler

8. PERFORMING ORGANIZATION REPORT NO.

9. PERFORMING ORGANIZATION NAME AND ADDRESS
See block 12.

10. PROGRAM ELEMENT NO.

11. CONTRACT/GRANT NO.
NA (Inhouse)

12. SPONSORING AGENCY NAME AND ADDRESS
EPA, Office of Research and Development
Industrial Environmental Research Laboratory
Research Triangle Park, NC 27711

13. TYPE OF REPORT AND PERIOD COVERED
Proceedings; 7/81

14. SPONSORING AGENCY CODE
EPA/600/13

15. SUPPLEMENTARY NOTES IERL-RTP project officer is J. David Mobley, Mail Drop 61, 919/541-2578.

16. ABSTRACT The proceedings document presentations made during an EPA-sponsored industry briefing, July 15, 1981, in Springfield, MO. The briefing dealt with the status of EPA's research activities on the adipic-acid-enhanced limestone flue gas desulfurization (FGD) process. Subjects covered included: (1) an overview of the adipic-acid-enhanced process, (2) the status of the demonstration project at Springfield City Utilities, (3) results of the demonstration project on an industrial boiler, (4) results of testing at the EPA prototype test facility at TVA's Shawnee steam plant, and (5) economics of limestone FGD systems using adipic acid. The briefing provided users, architects, engineers, vendors, consultants, and government personnel with a comprehensive assessment of this innovative technology for controlling SO2 emissions.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group	
Pollution	Gas Scrubbing	Pollution Control	13B	13H
Adipic Acid	Economic Analysis	Stationary Sources	07C	05C
Flue Gases			21B	
Desulfurization			07A,07D	
Calcium Carbonates			07B	
Scrubbers			13I	

18. DISTRIBUTION STATEMENT
Release to Public

19. SECURITY CLASS (This Report)
Unclassified

20. SECURITY CLASS (This page)
Unclassified

21. NO. OF PAGES
145

22. PRICE

EPA Form 2220-1 (9-73)

NOTICE

THIS DOCUMENT HAS BEEN REPRODUCED FROM THE BEST COPY FURNISHED US BY THE SPONSORING AGENCY. ALTHOUGH IT IS RECOGNIZED THAT CERTAIN PORTIONS ARE ILLEGIBLE, IT IS BEING RELEASED IN THE INTEREST OF MAKING AVAILABLE AS MUCH INFORMATION AS POSSIBLE.

EPA-600/9-82-012
June 1982

PROCEEDINGS: EPA'S INDUSTRY BRIEFING ON THE ADIPIC ACID ENHANCED LIMESTONE FGD PROCESS (JULY 1981)

J. David Mobley, Briefing Chairman

Industrial Environmental Research Laboratory
Office of Environmental Engineering and Technology
Research Triangle Park, North Carolina 27711

Prepared for

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Research and Development
Washington, D.C. 20460

1-b

PREFACE

EPA's Industrial Environmental Research Laboratory in Research Triangle Park, NC (IERL-RTP) periodically sponsors symposia and Industry Briefings for the transfer of information regarding research, development, and application activities with the objective of further accelerating the development and commercialization of technology. One of the major IERL-RTP efforts for the past several years has been advancement of the technology for flue gas desulfurization (FGD). A key element of the FGD program has been the advancement of lime/limestone wet scrubbing technology, which has led to the development of the adipic acid enhanced limestone FGD process.

The July 15, 1981 Industry Briefing was designed to provide interested people with EPA's latest findings on the use of adipic acid in lime/limestone scrubbers. The presentations covered testing work performed at the laboratory, bench, pilot, prototype, industrial, and utility scales. In addition, an economic assessment of the use of the technology on new and retrofit systems was included. The presentations were complemented by a tour of the FGD system at Springfield City Utilities' Southwest Power Station in Springfield, MO.

During the tour the FGD system was operating with the addition of approximately 1500 ppm of adipic acid. The scrubber was operating at 5.5 pH with a liquid to gas ratio of about 60 gal/1000 ft^3. The boiler was operating at 75% of maximum load with uncontrolled emissions of 6.5 lb/10^6 Btu. The emissions after the scrubber were 0.3 lb/10^6 Btu/lb which represents a SO_2 removal efficiency of over 95%. The SO_2 removal efficiency of the unit under similar operating conditions but without the adipic acid additive had previously been measured at about 70%.

More than 120 people representing electric utilities, industrial sources, architect and engineering firms, vendors, consultants, and governmental personnel attended the Conference. The Chairman of the Briefing was J. David Mobley, an Environmental Engineer with the Industrial Environmental Research Laboratory.

These Proceedings are comprised of copies of the participating authors' papers as received.

ABSTRACT

The proceedings document presentations made during an EPA sponsored industry briefing which was held on July 15, 1981 in Springfield, Missouri. The briefing dealt with the status of EPA's research activities on the adipic acid enhanced limestone flue gas desulfurization process. Subjects covered included: (1) overview of the adipic acid enhanced process, (2) status of the demonstration project at Springfield City Utilities, (3) results of the demonstration project on an industrial boiler, (4) results of testing at the EPA prototype test facility at TVA's Shawnee Steam Plant, and (5) economics of limestone flue gas desulfurization systems using adipic acid. The briefing provided users, architects and engineers, vendors, consultants, and government personnel with a comprehensive assessment of this innovative technology for controlling sulfur dioxide emissions.

CONTENTS

Page

Preface ii
Abstract iii
Acknowledgements v
Agenda vi

OVERVIEW OF EPA'S TESTING OF THE ADIPIC ACID ENHANCED LIMESTONE FGD PROCESS 1

J. C. S. Chang
J. D. Mobley

STATUS OF ADIPIC ACID ENHANCED FGD SYSTEM DEMONSTRATION AT SPRINGFIELD CITY UTILITIES SOUTHWEST POWER PLANT 19

O. W. Hargrove
J. D. Colley
G. E. Brown

EVALUATION OF THE ADIPIC ACID ENHANCED LIMESTONE FLUE GAS DESULFURIZATION PROCESS ON AN INDUSTRIAL BOILER 53

R. W. Gerstle
D. S. Henzel
J. D. Mobley

ADIPIC ACID-ENHANCED LIME/LIMESTONE TEST RESULTS AT THE EPA ALKALI SCRUBBING TEST FACILITY 75

S. C. Wang
D. A. Burbank

ECONOMICS OF LIMESTONE FGD SYSTEMS USING ADIPIC ACID 119

R. L. Torstrick
C. D. Stephenson
J. D. Veitch

APPENDIX: Attendees 133

ACKNOWLEDGEMENTS

The Chairman of the Briefing would like to acknowledge the support of the authors and speakers at the Briefing. In addition, the support of Springfield City Utilities is gratefully acknowledged for hosting the tour of the flue gas desulfurization system at their Southwest Power Station. Bruce T. Stone and N. Dale Hicks contributed significantly to the success of this endeavor. Personnel of the Radian Corporation were also very instrumental in the organization and conduct of the Briefing. In particular, the contributions of O. W. "Buddy" Hargrove, Jr., Pattie Dringenberg, James C. Dickerman, and J. David Colley were especially significant.

AGENDA

EPA's Industry Briefing on the Adipic Acid Enhanced Limestone FGD Process

Springfield, Missouri
July 15, 1981

7:30 - 8:30	Registration
8:30 - 8:35	Opening Comments M. A. Maxwell (EPA)
8:35 - 8:40	Welcome N. D. Hicks (Springfield City Utilities)
8:40 - 9:00	Overview of Adipic Acid Testing J. D. Mobley (EPA)
9:00 - 9:45	Results of Commercial Demonstration at Springfield O. W. Hargrove (Radian)
9:45 - 10:15	Break
10:15 - 10:30	Results of Rickenbacker Testing J. D. Mobley (EPA)
10:30 - 11:00	Results of Shawnee Testing D. A. Burbank (Bechtel)
11:00 - 11:30	Results of Economic Evaluation R. L. Torstrick (TVA)
11:30 - 11:45	Open Discussion
11:45 - 12:45	Lunch
	Tour of the FGD System at Springfield City Utilities' Southwest Power Plant
12:45 - 3:00	1st Tour Group - Buses will depart Hilton at 12:45; Buses will arrive at Airport (2:45) and Hotel (3:00)
1:45 - 4:00	2nd Tour Group - Buses will depart Hilton at 1:45; Buses will arrive at Airport (3:45) and Hotel (4:00)

AGENDA

EPA's Industry Briefing on the Adipic Acid Enhanced Limestone FGD Process

Springfield, Missouri
July 15, 1981

7:30 - 8:30	Registration
8:30 - 8:35	Opening Comments M. A. Maxwell (EPA)
8:35 - 8:40	Welcome N. D. Hicks (Springfield City Utilities)
8:40 - 9:00	Overview of Adipic Acid Testing J. D. Mobley (EPA)
9:00 - 9:45	Results of Commercial Demonstration at Springfield O. W. Hargrove (Radian)
9:45 - 10:15	Break
10:15 - 10:30	Results of Rickenbacker Testing J. D. Mobley (EPA)
10:30 - 11:00	Results of Shawnee Testing D. A. Burbank (Bechtel)
11:00 - 11:30	Results of Economic Evaluation R. L. Torstrick (TVA)
11:30 - 11:45	Open Discussion
11:45 - 12:45	Lunch
	Tour of the FGD System at Springfield City Utilities' Southwest Power Plant
12:45 - 3:00	1st Tour Group - Buses will depart Hilton at 12:45; Buses will arrive at Airport (2:45) and Hotel (3:00)
1:45 - 4:00	2nd Tour Group - Buses will depart Hilton at 1:45; Buses will arrive at Airport (3:45) and Hotel (4:00)

OVERVIEW OF EPA'S TESTING OF THE ADIPIC ACID ENHANCED LIMESTONE FGD PROCESS

Prepared by:

John C.S. Chang
Acurex Corporation
P. O. Box 13109
Research Triangle Park, NC 27709

and

J. David Mobley
Industrial Environmental Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

EPA Contract No. 68-02-3648

Presented at:

EPA's Industry Briefing on the
Adipic Acid Enhanced Limestone FGD Process

Springfield, MO
July 15, 1981

Overview of EPA's Testing of the Adipic Acid Enhanced Limestone FGD Process

ABSTRACT

Extensive research has determined that adipic acid, when used as an additive to a limestone flue gas desulfurization (FGD) system, will improve the performance of the system. Both SO_2 removal and limestone utilization can be greatly increased by the buffering effect of adipic acid. Extensive test data show that the technology is ready for full scale application. Although adipic acid does degrade in the scrubber, no significant operating problems or environmental impacts have been identified. Economic estimates have shown the adipic acid enhanced limestone FGD system to be economically attractive when compared to conventional FGD systems. In addition, further research is underway to decrease the cost of using additives in FGD systems.

Overview of EPA's Testing of the Adipic Acid Enhanced Limestone FGD Process

Introduction

The majority of FGD systems that are either operating or under planning for utility use are calcium-based lime or limestone processes because of the system simplicity and economics (Smith et al., 1981). Since lime is produced from limestone by an energy intensive calcination process, the direct use of limestone is becoming more attractive with the rising cost of energy. However, the performance of limestone scrubbers has been limited by reagent reactivity which results in low SO_2 removal efficiency, poor limestone utilization, and the ensuing reliability problems.

Extensive research has been conducted in the search for mass transfer enhancement additives that improve limestone scrubber performance. Adipic acid ($HOOC(CH_2)_4COOH$) was selected as the most attractive additive for research, development, and demonstration activities. Furthermore, it was found that the function of adipic acid is not adversely affected by forced oxidation and high chloride concentration. This gives the adipic acid enhanced limestone process advantages over other systems, such as the magnesium oxide promoted lime process, and makes it more suitable for closed-loop operation. Adipic acid has been tested in pilot-scale, prototype-scale, and full-scale limestone scrubbers and has demonstrated consistent improvement of system performance. The data indicate that the major benefits of adipic acid addition include:

- Increased SO_2 removal
- Decreased limestone consumption
- Decreased waste sludge volume
- Reduced operating cost
- Expanded FGD system flexibility

In addition, the adipic acid enhancement promotes the use of less expensive and less energy intensive limestone instead of lime. Further economic benefits can be obtained by the combustion of higher sulfur, less expensive coal without additional FGD equipment.

In order to promote this more advanced and more economical air pollution control technology and properly address the related environmental concerns, EPA's Industrial Environmental Research Laboratory-RTP (IERL-RTP) has conducted a comprehensive adipic acid program which has included the following six areas:

- Laboratory/theoretical investigation
- Scrubber testing and full-scale demonstration
- Degradation study
- Environmental impact and toxicity assessment
- Economic evaluation
- Alternative additives

The objectives of this paper are to report the highlights of EPA's adipic acid program and to discuss the recent development of the adipic acid enhanced limestone FGD process.

Laboratory/Theoretical Investigation

The major objectives of the laboratory/theoretical investigation were to understand the basic function of organic acid additives in limestone scrubbers and to search for the optimum additive.

Chemically speaking, limestone scrubber performance was limited by two pH extremes: (1) low pH near the gas/liquid interface which decreases the SO_2 solubility and absorption rate; (2) high pH near the liquid/solid interface which lowers the limestone solubility and dissolution rate. The basic chemical concepts show that this predicament can be relieved by the application of a buffer additive which can moderate the slurry pH and thus enhance the solubilities and mass transfer rates. TVA conducted the initial laboratory work and the data indicated some promise for an organic acid enhanced system (Hatfield and Potts, 1971). Rochelle (1977a, 1977b) performed a theoretical analysis and suggested the following criteria for the selection of organic acid additives:

- Proper solubility
- Low volatility
- Chemical stability
- No toxicity
- High availability
- Low cost

Under the sponsorship of EPA, Chang and Rochelle (1980) developed a mass transfer model and evaluated 11 potential organic acid additives (Chang, 1979). Table 1 shows the relative effectiveness and costs predicted by the model. It is shown that acetic and formic acids are the least expensive potential additives but their expected high volatility may result in significant losses which would increase the probability of having significant economic and environmental impacts. Phthalic acid also appears to be attractive but is more likely to result in environmental problems because of its aromatic structure. Lactic, benzoic, glycolic, and succinic acids are economically unattractive because of their high costs. Sulfopropionic, β-hydroxypropionic, sulfosuccinic, and adipic acids were found to have suitable properties as buffer additives. However, the former three are not readily available in large quantities from the chemical marketplace. Therefore, adipic acid was selected as the most attractive organic acid additive.

Table 1. Comparison of the effectiveness and costs of 11 potential organic acid additives (Chang, 1979)

Organic acid	Concentration required[a] (mM)	Price[b] ($/lb-mole)	Relative Cost
Acetic	14.3	11.4	0.37
Formic	17.7	12.9	0.51
Sulfosuccinic	7.8	44.1[c]	0.77
Phthalic	6.4	58.1[d]	0.84
β-hydroxypropionic	14.5	28.8[e]	0.94
Adipic	7.0	63.5	1.00
Sulfopropionic	16.1	28.8[e]	1.04
Benzoic	15.8	36.7	1.30
Glycolic	22.4	30.4	1.53
Succinic	7.3	106.0[f]	1.74
Lactic	24.7	73.8	4.10

---

[a] Basis: SO_2 removal equivalent to 7 mM of adipic acid enhancement

[b] Chemical Marketing Reporter, July 2, 1979

[c] Maleic anhydride

[d] Phthalic anhydride

[e] Acrylic acid

[f] Succinic anhydride

The mass transfer model simulated the adipic acid function in limestone scrubbing by considering the following reactions:

$$\text{Sulfur dioxide + Water} \rightleftarrows \text{Acidity + Sulfites} \tag{1}$$

$$[SO_2 + H_2O \rightleftarrows H^+ + HSO_3^-]$$

$$\text{Adipate ion + Acidity} \rightleftarrows \text{Adipic acid} \tag{2}$$

$$[^-OOC(CH_2)_4COO^- + 2H^+ \rightleftarrows HOOC(CH_2)_4COOH]$$

Reactions (1) and (2) show the buffering effect of adipic acid. As adipate ions react with the acidity (2) generated by the absorption of SO_2 (1), reaction (1) is shifted to the right and the SO_2 removal efficiency is enhanced. The mass transfer model predicted that less than 3000 ppm of adipic acid should be appropriate for significant SO_2 removal enhancement. The model also predicted that the SO_2 absorption rate would be higher under forced oxidation conditions due to less interference by the bisulfite ion. These two predictions were verified by data from actual scrubber testing (Borgwardt, 1978; Burbank et al., 1981).

Chan and Rochelle (1981) recently developed a theoretical model to describe the adipic acid function on limestone dissolution mechanism by the following two major reactions:

$$\text{Limestone + Water} \rightarrow \text{Alkalinity + Calcium ion + Carbonates} \tag{3}$$

$$[CaCO_3 + H_2O \rightarrow OH^- + Ca^{++} + HCO_3^-]$$

$$\text{Adipic acid + Alkalinity} \rightleftarrows \text{Adipate ion + Water} \tag{4}$$

$$[HOOC(CH_2)_4COOH + 2OH^- \rightleftarrows {}^-OOC(CH_2)_4COO^- + 2H_2O]$$

Equations (3) and (4) show that the adipate ions consumed by buffering the absorbed SO_2 as shown in Reactions (1) and (2) are replenished as alkalinity is generated by limestone dissolution. Due to those reactions, no adipic acid is consumed and the limestone dissolution rate is enhanced by the buffering effect. Laboratory experiments confirmed that the limestone dissolution rate was significantly increased by adipic acid as shown in Figure 1.

Scrubber Testing and Full-Scale Demonstration

In order to examine the technical and economic feasibility of adipic acid enhanced FGD systems, IERL-RTP has conducted a series of scrubber tests consisting of bench (0.6 kW), pilot (0.1 MW), prototype (10 MW), and commercial (20 and 200 MW) scale. It can be seen from Table 2 and Figure 2 that the adipic acid technology has been tested in a variety of scrubber sizes, types, operation modes, and operating conditions. The major results are summarized as follows:

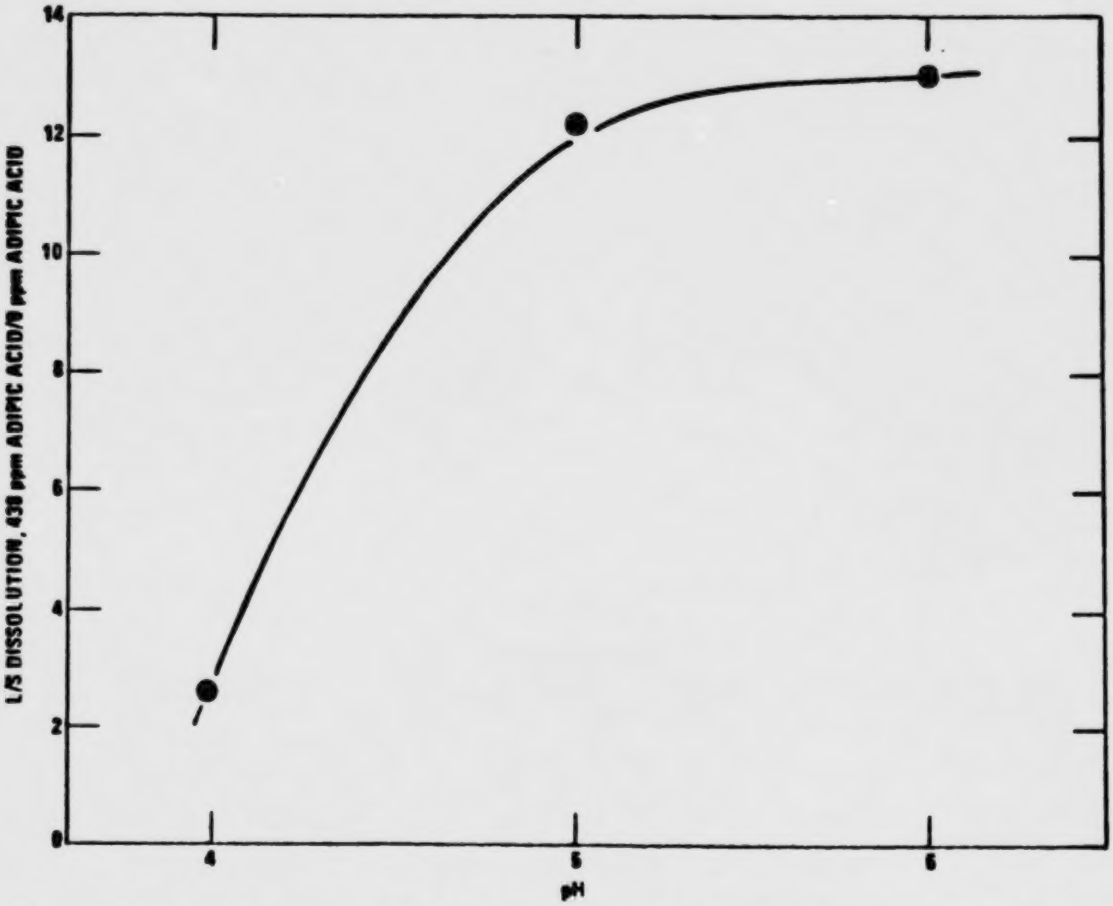


Figure 1. Ratio of limestone dissolution rate with and without adipic acid enhancement in 0.1 M $CaCl_2$ with N_2 sparging at 25° C (Chan and Rochelle, 1981).

Table 2. Major operating ranges of adipic acid scrubber testing

Adipic acid concentration, ppm	0 - 4200
Cl, ppm	0 - 17,000
Na, ppm	0 - 22,000
SO_2 (gas), ppm	1500 - 2900
Hold tank pH	4.6 - 6.2
L/G, $1/m^3$ (gal./kcf)	2 - 12 (15 - 90)
Fly ash loading, g/m^3 (gr/dscf)	0 - 13 (0 - 6)

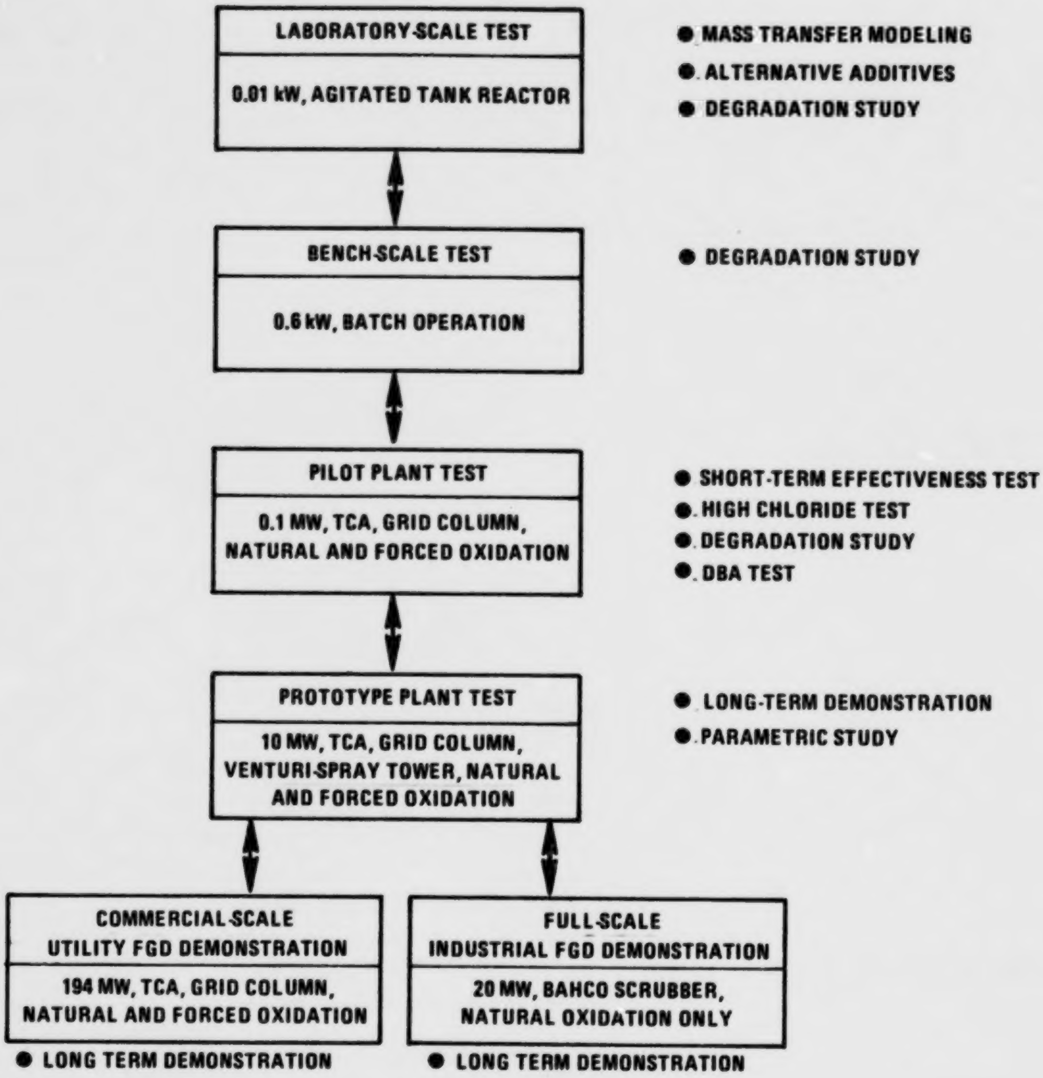

LABORATORY-SCALE TEST
0.01 kW, AGITATED TANK REACTOR
● MASS TRANSFER MODELING
● ALTERNATIVE ADDITIVES
● DEGRADATION STUDY
BENCH-SCALE TEST
0.6 kW, BATCH OPERATION
● DEGRADATION STUDY
PILOT PLANT TEST
0.1 MW, TCA, GRID COLUMN, NATURAL AND FORCED OXIDATION
● SHORT-TERM EFFECTIVENESS TEST
● HIGH CHLORIDE TEST
● DEGRADATION STUDY
● DBA TEST
PROTOTYPE PLANT TEST
10 MW, TCA, GRID COLUMN, VENTURI-SPRAY TOWER, NATURAL AND FORCED OXIDATION
● LONG-TERM DEMONSTRATION
● PARAMETRIC STUDY
COMMERCIAL-SCALE UTILITY FGD DEMONSTRATION
194 MW, TCA, GRID COLUMN, NATURAL AND FORCED OXIDATION
● LONG TERM DEMONSTRATION
FULL-SCALE INDUSTRIAL FGD DEMONSTRATION
20 MW, BAHCO SCRUBBER, NATURAL OXIDATION ONLY
● LONG TERM DEMONSTRATION

Figure 2. Scenario of adipic acid scrubber testing and full-scale demonstration.

- SO_2 removal efficiency - A significant increase of SO_2 removal was observed at every level of scrubber testing. The data show that small amounts of adipic acid are required to raise the SO_2 removal efficiency from 50 to over 95 percent. The recent full-scale demonstration showed that 90 percent SO_2 removal was attained in a Turbulent Contact Absorber (TCA) without packing spheres with the addition of 2500 ppm adipic acid (Figure 3) (Hargrove, 1981).

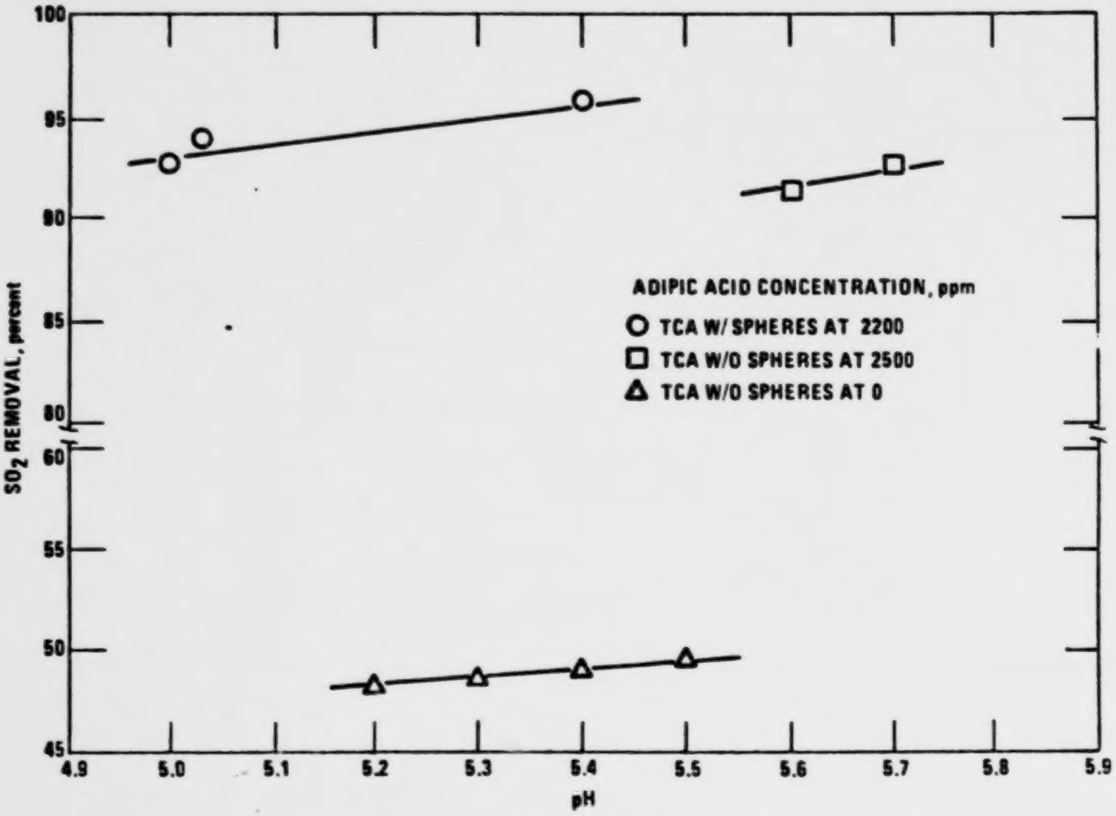


Figure 3. Scrubber performance of full scale TCA (200 MW) with and without packing spheres (Hargrove, 1981).

- Limestone utilization - A limestone utilization of more than 90 percent was achieved without sacrificing SO_2 removal efficiency. Adipic acid addition allowed operation of the limestone scrubbers at a lower pH range (4.8-5.5) which results in high limestone utilization, low scaling tendency and high reaction gain for automatic pH control (Garrett, 1981).

- High chloride testing - No significant difference in SO_2 removal was observed between runs at the IERL-RTP pilot plant with low (450 ppm) and high (13,000 ppm) concentrations of chloride (Borgwardt and Dene, 1977a). The effectiveness of adipic acid in the presence of high chloride concentrations is an important factor since other additives, such as magnesium, are adversely affected by chlorides. The results of the tests confirm the suitability of adipic acid as an additive to closed-loop scrubber operation.

- Forced oxidation - The capability of forced oxidation to produce high quality waste sludge is another advantage of adipic acid enhancement over other additives such as sodium and magnesium. The prototype scrubber testing showed that the total adipic acid consumption rate is not significantly different between natural and forced oxidation conditions (Burbank et al., 1980, Borgwardt and Dene, 1977b).

- Long-term demonstration - Several long term (35 to 70 days), high performance adipic acid tests were carried out with both prototype and full-scale scrubbers. Continuous, smooth operation was sustained throughout each run without major operating problems. The data showed that adipic acid enhanced scrubbers can provide constant high performance under the normal load fluctuations experienced with the peaking operations of power plants (Bechtel, 1981).

Degradation Study

A material balance showed that an unaccounted-for adipic acid loss was occurring in scrubber testing (Chang, 1981). Laboratory research has shown that the unaccounted-for losses were primarily caused by two mechanisms: (1) chemical degradation of adipic acid; and (2) occlusion of adipic acid and its degradation products in the precipitated calcium sulfite/sulfate solids. The first mechanism is responsible for most of the loss, especially under forced oxidation conditions.

The principal products of the degradation are glutaric acid ($HOOC(CH_2)_3COOH$), valeric acid ($CH_3(CH_2)_3COOH$), and carbon dioxide. The valeric acid has a musty odor which is somewhat unpleasant; however, its concentration as a degradation product in the scrubber liquor is so low that the odor has not been a problem in testing to date. Other products that have been identified in trace amounts are succinic acid, propane, butane, methane, and carbon monoxide. Typical concentration of these products, measured at the prototype plant, is shown in Table 3 (Meserole et al., 1979). Theoretical analysis indicated that the degradation probably results from decarboxylation as the acid reacts with free radicals produced by oxidation of absorbed SO_2. This oxidative decarboxylation of adipic acid produces shorter molecules with fewer carbon atoms in the chain.

Table 3. Carbon compounds identified in scrubber when using adipic acid additive (Meserole et al., 1979)

	Adipic acid	Glutaric acid	Valeric acid	Succinic acid	CO^a
Natural oxidation					
Liquid, mg/l	1,500	120	30	2	nd
Solid, μg/g	820	200	<5	<4	
Forced oxidation					
Liquid, mg/l	1,600	150	30	40	40
Solid, μg/g	40	<4	<5	<4	

---

[a] in oxidizer vent gas, ppm

nd - not detected

Laboratory and bench-scale experiments showed that adipic acid degradation is affected by several important factors: degree of oxidation, temperature, adipic acid concentration, and inhibitors (Rochelle et al., 1981; Jarvis and Schubert, 1981). Forced oxidation accelerates the degradation rate but does not increase the adipic acid consumption in full-scale scrubbers because the degradation loss is more than compensated by tighter water balances and less occlusion losses. The degradation inhibition effect of manganous ion at a pH below 5.0 was first verified at the University of Texas at Austin's laboratory and IERL-RTP's pilot plant (Rochelle et al., 1981; Chang, 1981). The presence of manganous ion is known to alter the mechanism of free radical initiation and propagation during SO_2 oxidation and probably results in fewer radicals in the limestone slurry. Research at the University of Texas at Austin, under an EPA cooperative agreement, showed that 10 to 15 ppm of manganous ion present at pH 4.6 can reduce the adipic acid degradation rate by two thirds (Rochelle et al., 1981). Data from bench-scale scrubber field studies confirmed the manganous ion effect under both natural and forced oxidation conditions (Jarvis and Schubert, 1981). Analysis of slurry samples from the prototype plant showed that manganese concentration, probably leached from the fly ash, accumulated up to 57 ppm (Bechtel, 1980).

Environmental Impact and Toxicity Assessment

No significant incremental environmental impact is anticipated when adipic acid is used as an additive in limestone scrubbers. The low concentrations of adipic acid in limestone slurries minimize any possibility of secondary environmental impacts.

In order to determine if solid waste from adipic acid enhanced limestone scrubbers should be classified as a hazardous waste, sludge samples from the prototype plant were analyzed according to the Extraction Procedure Toxicity Test as prescribed by regulations pursuant to the Resource Conservation and Recovery Act (RCRA). The results of the analysis are listed in Table 4 (Epler et al., 1979). It is seen that most of the elements are not significantly different between extracts from sludges with and without adipic acid and that they are all considerably lower than the concentration deemed hazardous.

Table 4. Results of extraction procedure toxicity test (Epler et al., 1979)

Extract	Concentration of element (μg/l)							
	Ag	As	Ba	Cd	Cr	Hg	Pb	Se
Sludge of limestone scrubber	1	47	<500	2	10	0.1	2	30
Sludge of adipic acid enhanced limestone scrubber	<1	54	<500	4	13	0.1	3	43
Hazardous waste criteria[a]	5,000	5,000	100,000	1,000	5,000	200	5,000	5,000

---

[a] Federal Register/Vol. 45, No. 98/Monday, May 19, 1980.

In order to further evaluate the impact of adipic acid addition, chemical and biological tests were conducted on samples from the prototype scrubber while operating with and without adipic acid addition. Samples were taken from the flue gas after the scrubber, the oxidation tank vent, the scrubber slurry, and the filter cake. The chemical tests included the standard Level 1 test series (Lentzen et al., 1978). The only significant difference in the chemical analysis was that more polar organic material was emitted in the flue gas from the adipic acid enhanced system (Barbour et al., 1980); however, the level emitted does not constitute an environmental problem. The biological tests included: (1) the mutagenicity assay, (2) CHO clonal toxicity assay, (3) rabbit alveolar macrophage (RAM) cytotoxicity assay, (4) human cell cytotoxicity assay, (5) rodent toxicity, and (6) fresh water toxicity assay on algae, fish, and invertibrates. There was no significant difference in toxicity or mutagenicity between the samples containing adipic acid and its degradation products and samples from conventional limestone systems (Litton, 1979). Confirmatory genetic toxicity assays were also conducted on the leachate from adipic acid enhanced and conventional limestone FGD systems. The tests included salmonella/microsome assay, saccharomyces can^r/his$^+$ dual assay, and salmonella uvrB repair assay. The results from these tests showed no genetic activity in the samples (Epler et al., 1979).

It should be noted that adipic acid is included on the hazardous substances list which was promulgated by EPA pursuant to the Clean Water Act. This list was developed primarily to identify substances, which if discharged into lakes, rivers, and streams in sufficient quantities, would be toxic to aquatic organisms. The regulations require notification of EPA in the event of a discharge of the substance in greater than the designated reportable quantity. The reportable quantity for a discharge of adipic acid, as well as lime, is 2270 kg (5000 lb). The fact that adipic acid is one of about 300 chemicals appearing on the hazardous substances list does not restrict its use in the nylon industry or even as a food additive. Likewise, it does not affect the use of adipic acid as an additive to FGD systems.

Worker exposure to adipic acid is not a problem. Dust inhalation can be controlled by a filter mask if necessary. The item most often associated with using adipic acid in FGD systems is the unpleasant odor which has been reported. The odor is probably a result of adipic acid's being degraded to valeric acid which has a very low threshold for odor detection. The odor has been reported occasionally at Shawnee and Springfield; however, it has not been a problem at either location. The odor was not noticed in the testing at Rickenbacker. The odor, or possibility thereof, should not constrain use of adipic acid in FGD systems.

Economic Evaluation

Based upon the data of prototype adipic acid testing, several economic comparisons of limestone FGD systems with and without adipic acid enhancement have been prepared (Burbank et al., 1981; McGlamery et al., 1981). These estimates show that for a new system with a 90-95 percent SO_2 removal requirement, both operating and capital costs for adipic acid enhanced systems are less than for conventional limestone systems. The lower costs for the adipic acid enhanced system are due to energy savings and to the reduced amount of limestone and solid waste. These projections do not incorporate any economic benefit to the increased operability and potentially decreased maintenance that would be expected with an adipic acid system. Further, economic benefits can potentially be accrued by burning higher sulfur, less expensive coal or from converting lime to limestone systems. In addition, systems with compliance problems may retrofit adipic acid addition relatively easily and bring a system into compliance with a minimal capital expenditure and in a brief period of time. Therefore, site specific factors may make use of adipic acid very attractive.

Alternative Additives

In order to pursue more economic and chemically stable additives, IERL-RTP is conducting research on two promising buffers--dibasic acid (DBA) residue and glycolic acid.

DBA is the waste material or by-product of adipic acid or cyclohexanone manufacturing processes which contains an appreciable amount of organic acids. The market price of DBA is expected to be 40 to 50 percent cheaper than pure adipic acid. Four dibasic acids are currently being tested at IERL-RTP's pilot plant to evaluate and compare the effectiveness of DBA with pure adipic acid in terms of SO_2 removal efficiency and limestone utilization (Chang and Dempsey, 1981). The preliminary results (Figure 4) show that DBA significantly enhances the SO_2 removal efficiency. If "meq/liter" is taken as the basis of organic acid concentration, equivalent scrubber performance can be obtained between DBA and pure adipic acid promoted limestone systems. Further testing is scheduled to evaluate the degradation rate, toxicity, and economics of the DBA enhanced limestone systems.

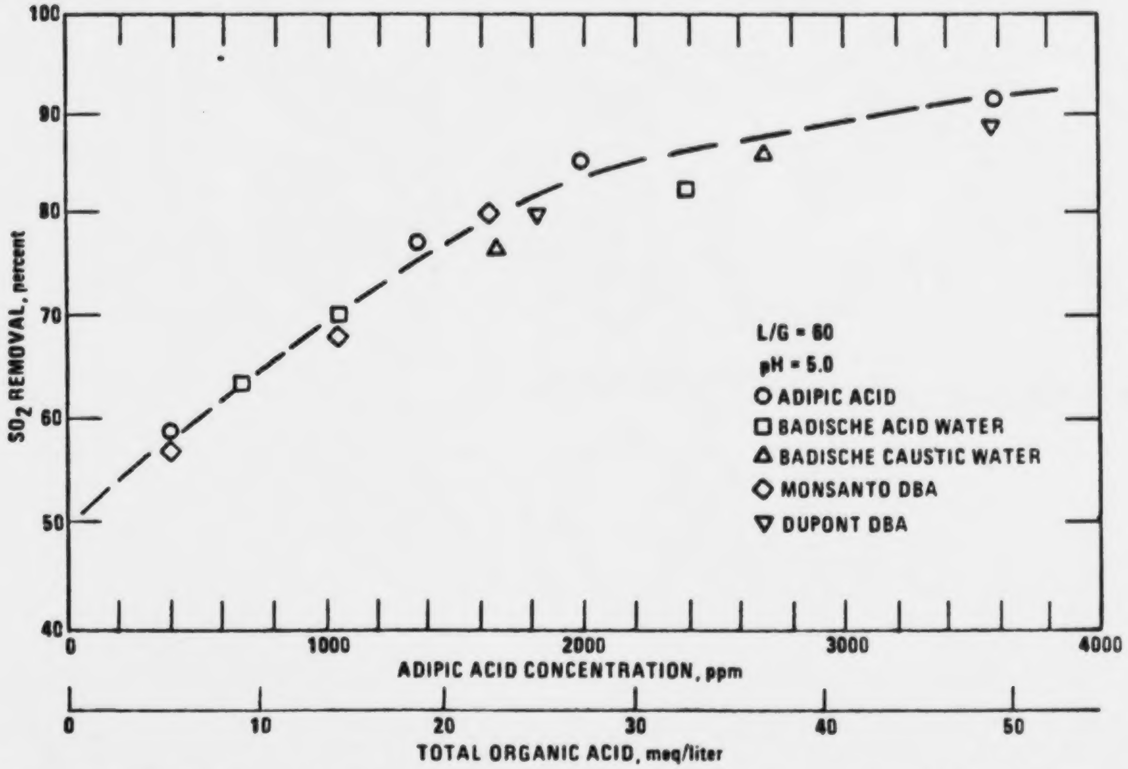


Figure 4. Effect of organic acid concentration on sulfur dioxide removal at the RTP pilot plant (Chang and Dempsey, 1981).

Laboratory studies showed that glycolic acid ($HOCH_2COOH$) is not subject to chemical degradation under simulated scrubber conditions. Pilot plant testing is under consideration to investigate the potential benefits of this non-degradable additive.

Summary

The following conclusions are drawn from this review of the EPA adipic acid program:

(1) Adipic acid is an effective mass transfer enhancement additive for wet limestone FGD systems. Both SO_2 removal and limestone utilization can be greatly increased by the buffering effect of less than 3000 ppm of adipic acid.

(2) Adipic acid enhanced FGD systems have been extensively tested in a variety of limestone systems. Data show that the technology is ready for full-scale application and most existing limestone FGD scrubbers should be able to benefit from adipic acid addition without major process changes.

(3) Adipic acid degradation is caused by oxidative decarboxylation. The degradation products did not pose any serious operating problems. Manganous ion leached from fly ash at a pH below 5.0 can reduce the adipic acid degradation rate.

(4) No significant environmental impact from adipic acid enhanced FGD systems is expected. The test results show no significant difference in toxicity or mutagenicity in samples containing adipic acid and its degradation products and samples from conventional limestone scrubbing.

(5) The addition of adipic acid should be economically attractive when compared to conventional FGD systems. Economic benefits can be derived from the savings on energy consumption, raw material, solid waste reduction, and shifting to less expensive coal and limestone.

(6) Research on other possible additives has identified waste dibasic acids and glycolic acid as potential additives for the enhancement of limestone FGD systems that provide benefits similar to adipic acid at a lower cost.

References

Barbour, Rachael, J.E. Howes, Jr., D.F. Kohler, A. Bjorseth, and M. Cooke, "Level 1 Assessment of Limestone Scrubbing with Adipic Acid Addition," Draft Final Report, Battelle Columbus Laboratories, Columbus, OH, June (1980).

Bechtel National, Inc., "EPA Alkali Scrubbing Test Facility TVA Shawnee Power Plant," Monthly Progress Report for May 1980, EPA Contract 68-02-3114, July 30 (1980).

Bechtel National, Inc. Ibid, for March 1981, May 19 (1981).

Borgwardt, R.H., "Effect of Forced Oxidation on Limestone/SO_x Scrubber Performance," In Proceedings: Symposium on Flue Gas Desulfurization--Hollywood, FL, November 1977 (Volume I), EPA-600/7-78-058a (NTIS PB 282090), p. 205 (1978).

Borgwardt, R.H., and C.E. Dene, "Limestone Scrubbing of SO_2 at EPA/RTP Pilot Plant," Progress Report No. 29, EPA Contract 68-02-2646, December (1977a).

Borgwardt, R.H., and C.E. Dene, Ibid, No. 28, November (1977b).

Burbank, D.A., S.C. Wang, R.R. McKinsey, and J.E. Williams, "Test Results on Adipic Acid-Enhanced Limestone Scrubbing at the EPA Shawnee Test Facility - Third Report," In Proceedings: Symposium on Flue Gas Desulfurization--Houston, October 1980: Volume 1, EPA-600/9-81-019a, April (1981).

Chan, P.K., and G.T. Rochelle, "Limestone Dissolution Effect of pH, CO_2 and Buffers Modeled by Mass Transfer," ACS National Meeting, Atlanta, GA, March 29-30 (1981).

Chang, C.S., "Mass Transfer with Equilibrium Chemical Reaction: Sulfur Dioxide Absorption in Aqueous Solutions," Ph.D. Dissertation, University of Texas at Austin, TX (1979).

Chang, C.S., and G.T. Rochelle, "SO_2 Absorption into $CaO/CaCO_3$ Slurries with Buffer Additives," AIChE 73rd National Meeting, Chicago, IL, November (1980).

Chang, C.S., "Effect of Scrubbing Operating Conditions on Adipic Acid Degradation," EPA-600/7-81-017 (NTIS PB 81-163305), February (1981).

Chang, C.S., and J.H. Dempsey, "Operation of EPA-Owned Pilot SO_2 Scrubbers," Progress Report for April 1981, EPA Contract 68-02-3648, Acurex Corporation, Research Triangle Park, NC, May 8 (1981).

Epler, J.L., et al., "Toxicity of Leachates," Draft Final Report, EPA-IAG-78-DX-0373, Oak Ridge National Laboratory, Oak Ridge, TN (1979).

Garrett, P., "Automation Investigation of Environmental Control Processes," Tenth Quarterly Report, EPA Grant RR80575803, University of Cincinnati, Cincinnati, OH, January (1981).

Hargrove, Jr., O.W., "Status of Adipic Acid Demonstration Program at Springfield, Missouri," EPA Contract 68-02-3191, Adipic Acid Coordination Meeting, RTP, NC, April 7 (1981).

Hatfield, J.D., and J.M. Potts, "Scrubbing with Limestone Slurry: Use of Organic Acids," Proceedings: Second International Lime/Limestone Wet Scrubbing Symposium, New Orleans, LA, EPA report APTD 1161 (1971).

Jarvis, J.B., and S.A. Schubert, "Effect of Trace Metals and Sulfite Oxidation on Adipic Acid Degradation," Technical Progress Report No. 2, EPA Contract 68-02-3171, Task 29, Radian Corporation, Austin, TX, March (1981).

Lentzen, D.E., D.E. Wagoner, E.D. Estes, and W.F. Gutknecht, "IERL-RTP Procedures Manual: Level 1 Environmental Assessment (Second Edition)," EPA-600/7-78-201 (NTIS PB 293795), October (1978).

Litton Bionetics, Inc., "Level 1 Bioassays on Nine Conventional Limestone Scrubbing Samples With and Without Adipic Acid Additive," EPA Contract 68-02-2681, Draft Final Report, October (1979).

McGlamery, G.G., W.E. O'Brien, C.D. Stephenson, and J.D. Veitch, "FGD Economics in 1980," In Proceedings: Symposium on Flue Gas Desulfurization--Houston, October 1980: Volume 1, EPA-600/9-81-019a, April (1981).

Meserole, F.B., D.L. Lewis, A.W. Nichols, and G.T. Rochelle, "Adipic Acid Degradation Mechanism in Aqueous FGD System," EPA/600-7-79-224 (NTIS PB 80-144595), September (1979).

Rochelle, G.T., and C.J. King, "Effect of Additives on Mass Transfer in $CaCO_3$ or CaO Slurry Scrubbing of SO_2 from Waste Gases," Ind. Eng. Chem. Fund. 16:67-75 (1977a).

Rochelle, G.T., "Process Synthesis and Innovation in Flue Gas Desulfurization," EPRI-FP-463-SR, July (1977b).

Rochelle, G.T., T.W. Williams, J.S. Raymond, and M.W. Hsiang, "Buffer Additives for Lime/Limestone Slurry Scrubbing," ACS National Meeting, Atlanta, GA, March 30-31 (1981).

Smith, M.P., M.T. Melia, B.A. Laseke, Jr., and N. Kaplan, "Recent Trends in Utility Flue Gas Desulfurization," In Proceedings: Symposium on Flue Gas Desulfurization--Houston, October 1980: Volume 1, EPA-600/9-81-019a, April (1981).

STATUS OF ADIPIC ACID ENHANCED FGD SYSTEM
DEMONSTRATION AT SPRINGFIELD CITY UTILITIES SOUTHWEST POWER PLANT

Prepared by:

O. W. Hargrove, J. D. Colley, and G. E. Brown
Radian Corporation
P. O. Box 9948
Austin, TX 78766

EPA Project Officer:

J. David Mobley
Industrial Environmental Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

EPA Contract No. 68-02-3191

Presented at:

EPA's Industry Briefing on the
Adipic Acid Enhanced Limestone FGD Process

Springfield, MO
July 15, 1981

Preceding page blank

SUMMARY

Demonstration of adipic acid as an additive to enhance the performance of limestone FGD systems is proceeding quite successfully at Springfield City Utilities' Southwest Power Plant (SWPP). Both forced oxidation and natural oxidation testing were planned at Springfield. The forced oxidation tests were completed in late April and the natural oxidation should be completed in August. This paper focuses primarily on the forced oxidation test phase.

Two benefits quoted frequently are that adipic acid (1) improves SO_2 removal efficiency and (2) allows high limestone utilization to be achieved simultaneously with high SO_2 removals. SO_2 removal efficiencies greater than 90 percent were consistently achieved for over 35 days with adipic acid. This compares with SO_2 removal efficiencies of 50 to 60 percent without adipic acid. Limestone utilization was also typically about 90 percent.

In addition, both scrubbers operated for 36 days with only about 10 hours of downtime. This represents the longest period of continuous operation experienced at SWPP to date. The improved reliability can be attributed to design modifications and operating procedure changes implemented by City Utilities, additional process input by Radian, and process reliability factors created by adipic acid addition and forced oxidation. While the adipic acid certainly played a large role in the long-term run, the cooperation and responsiveness shown by City Utilities may have been an even larger factor.

PROCESS DESCRIPTION

Springfield City Utilities' Southwest Unit 1 is a 194 MW coal-fired unit designed to burn 3.5 to 4.0 percent sulfur coal. Figure 1 shows the flue gas flow scheme through the gas cleaning sections of the plant. After exiting the boiler, the gas passes through the air preheater, electrostatic precipitator, and induced draft fans prior to entering the FGD system and subsequently exiting the plant through the stack.

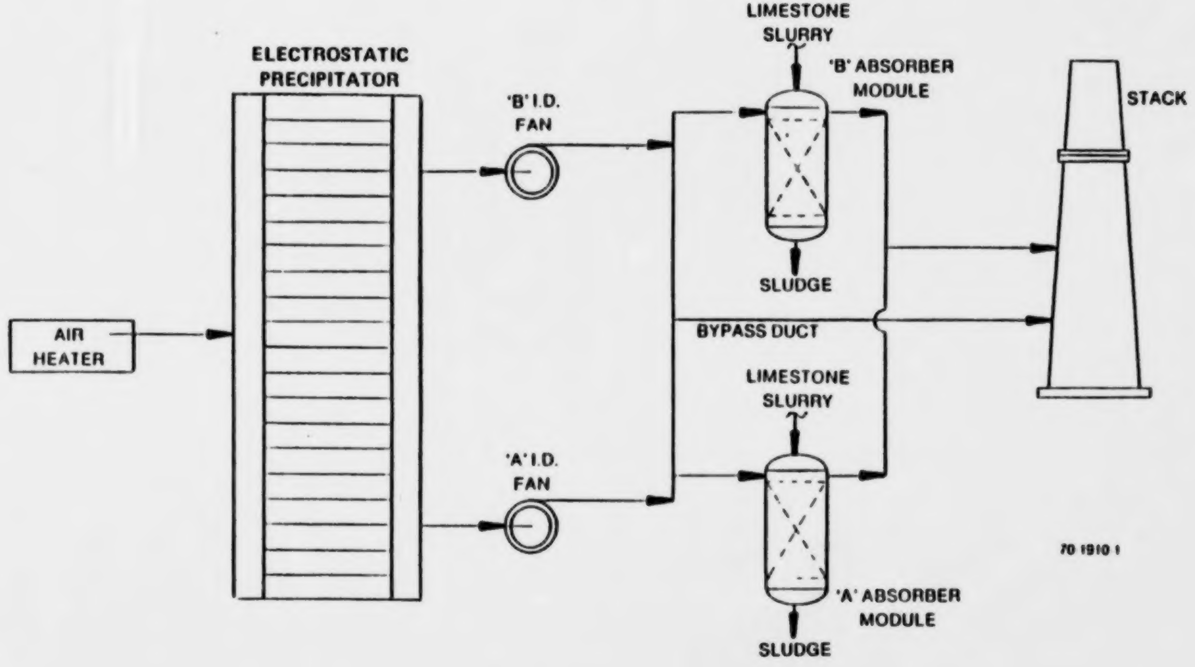

AIR HEATER
ELECTROSTATIC PRECIPITATOR
'B' I.D. FAN
'A' I.D. FAN
LIMESTONE SLURRY
'B' ABSORBER MODULE
SLUDGE
BYPASS DUCT
LIMESTONE SLURRY
'A' ABSORBER MODULE
SLUDGE
STACK
70 1910 1

Figure 1. Southwest Unit 1 flue gas flow schematic.

The FGD system consists of two parallel TCA scrubber modules, each sized to handle 60 percent of the design flue gas flow. Limestone preparation and sludge handling systems are common to the two TCA modules.

Figure 2 shows the flow schematic for one of the two TCA modules. The gas enters the presaturator area and is cooled by supernatent liquor (thickener overflow). The gas then passes through three levels of TCA spheres where SO_2 removal is accomplished, the mist eliminator, and out the stack. The lower bank of mist eliminator blades is washed continuously with supernatant liquor to minimize scaling and plugging problems.

Slurry is circulated from the reaction hold tank below the scrubber through spray nozzles above the top level of spheres. Makeup limestone is pumped from the limestone storage tank to the reaction tank to maintain the pH set point.

Waste from the hold tank is pumped to the thickener (Figure 3). Here the solids are allowed to settle, then filtered, mixed with fly ash, and trucked to a landfill.

Two relatively simple process modifications were made for the test program. First, an adipic acid feed system was installed to add adipic acid powder on a continuous basis. Adipic acid is delivered on-site in 1100 pound sacks. These sacks are loaded by an electric hoist into a two-ton Vibra Screw vibrating silo. The adipic acid is fed from the silo to a Vibra Screw volumetric live bin screw feeder by a Taunton screw conveyor. The adipic acid feed rate from the screw feeder into the limestone sump is set manually. After the adipic acid is mixed with the freshly ground limestone slurry from the ball mills, the mixture is pumped to the limestone storage tank. Since the limestone handling equipment is common to both scrubber modules, both scrubbers usually operate with the same adipic acid concentration.

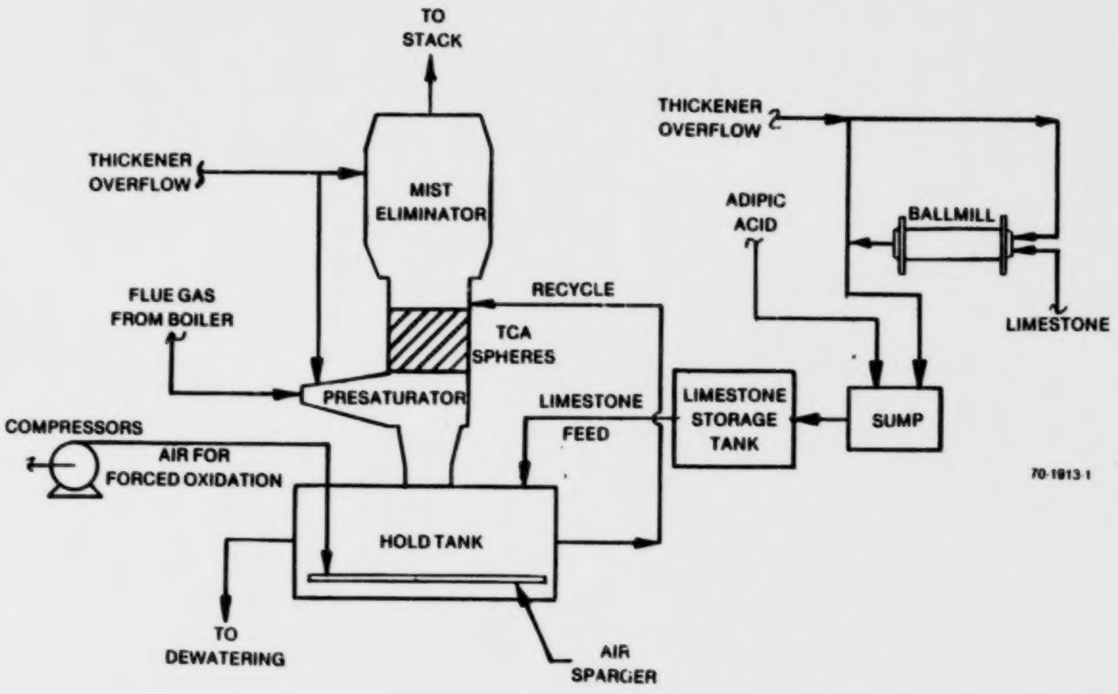

TO
STACK
THICKENER
OVERFLOW
MIST
ELIMINATOR
FLUE GAS
FROM BOILER
RECYCLE
TCA
SPHERES
PRESATURATOR
LIMESTONE
FEED
COMPRESSORS
AIR FOR
FORCED OXIDATION
HOLD TANK
TO
DEWATERING
AIR
SPARGER
THICKENER
OVERFLOW
ADIPIC
ACID
BALLMILL
LIMESTONE
LIMESTONE
STORAGE
TANK
SUMP
70-1913-1

Figure 2. Southwest Unit 1 scrubber module flow diagram.

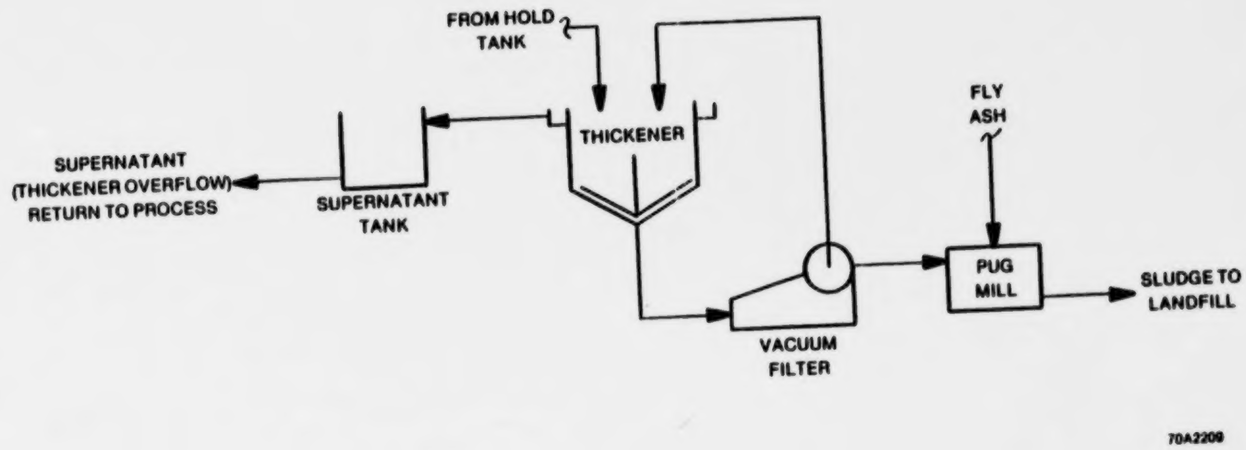

FROM HOLD TANK
THICKENER
FLY ASH
SUPERNATANT (THICKENER OVERFLOW) RETURN TO PROCESS
SUPERNATANT TANK
PUG MILL
SLUDGE TO LANDFILL
VACUUM FILTER
70A2209

Figure 3. Southwest Unit 1 dewatering plant schematic.

A second modification made for the forced oxidation test phase involved the addition of forced oxidation equipment. Four CENTAC CII-18M2 Ingersoll-Rand compressors were brought on-site for the duration of the forced oxidation testing. Each of the compressors was designed to deliver 1800 scfm into a common header. The air flow to either scrubber module could be controlled independently as long as the total air flow remained below 7200 scfm.

The air sparge assembly in each reaction tank consisted of 60 one inch diameter holes cut in the bottom of six inch carbon steel pipe installed in a rectangular configuration. The header was placed three feet from each wall of the reaction tank so that the rising air did not place additional stress on the agitator shaft. More typical design practice would be to place the sparge header in close proximity to the agitator, but this would have required upgrading the size of the agitator, shaft, gear box, and motor assembly on each reaction hold tank. The expense could not be justified for a three-month demonstration test duration. However, this design compromise means that agitator horsepower was not utilized to distribute the air so an optimum forced oxidation system was not demonstrated.

In addition to these process modifications, on-line gas analyzers were installed to monitor each scrubber module's performance. Two DuPont SO_2 analyzers and two Thermox O_2 analyzers were used to continuously monitor gas compositions. One set of DuPont/Thermox instruments was located between the two inlet ducts and alternately measured the inlet gas composition to each scrubber. Another set of instruments was placed between the outlet ducts to monitor the scrubbers' exit gases. A Radian DART® data acquisition system was installed in the scrubber control room to log the continuous monitoring results. A chart recorder was used as backup for the primary data acquisition system. The SO_2/O_2 analyzers and data acquisition system were certified in late January according to the proposed regulations set forth in the October 10, 1979 Federal Register.

PROGRAM GOALS

The objective of this demonstration program has been and continues to be to verify the findings at Shawnee on a full-scale utility scrubber. As a result, no parametric studies were planned, and emphasis was placed on long-term scrubber operation with a specified set of control points. The long-term tests were to determine the effect adipic acid addition has on system performance including the impact the additive has on system controllability and ease of operation.

The program was divided into two distinct three-month test phases, forced oxidation and natural oxidation test modes. Within each phase, a one-month baseline period and a two-month period for adipic acid testing were planned. The specific goals for each of these test phases are outlined below:

PROGRAM GOALS

Forced Oxidation

- Document performance of system without adipic acid (baseline tests).
- Document conditions required to meet 1.2 lbs SO_2/MM Btu without TCA spheres.
- Operate 30+ days at:
  - 95% SO_2 removal efficiency
  - 90% limestone utilization
  - 95% sulfite oxidation
  - minimum sulfite blinding of the limestone.
- Gather data with instruments certified according to EPA procedures.

Natural Oxidation

- Document system performance without adipic acid (baseline tests).
- Document conditions required to meet 1.2 lbs SO_2/MM Btu in TCA and tray modules.
- Operate 30+ days to achieve:
  - 95% SO_2 removal efficiency
  - 90% limestone utilization.
- Gather data with instruments certified according to EPA procedures.

Initial control set points were based on the Shawnee prototype test facility results and were modified as necessary to achieve the stated goals. Thus, conducting the test program provides a means of comparing data from a full-scale installation with the Shawnee data over a limited but meaningful set of operating conditions.

DISCUSSION OF RESULTS

The forced oxidation program goals were met or exceeded for the most part and the testing is judged to be quite successful. Although there are some differences between the Springfield test results and test results from Shawnee prototype testing, the trends from Shawnee were supported for the most part. As expected, most of the technical findings from Shawnee can be extrapolated to a commercial-scale system with few problems.

Major accomplishments during the forced oxidation/adipic acid testing include:

- Above 85 percent SO_2 removal with adipic acid and without TCA spheres in S-1 for a period of about one week.
- Improvement in SO_2 removal from 50-60 percent at baseline conditions to routinely above 90 percent including 14 consecutive days when both scrubbers averaged almost 95 percent removal.
- Limestone utilization in the 85 to 95 percent range.

- Sulfite oxidation efficiency of 94 percent (average) for Module S-2 over the course of the adipic acid testing.
- 36 days of virtually uninterrupted service for both scrubber modules (longest period when both scrubbers have been in service to date.)

Summary of FGD System Performance

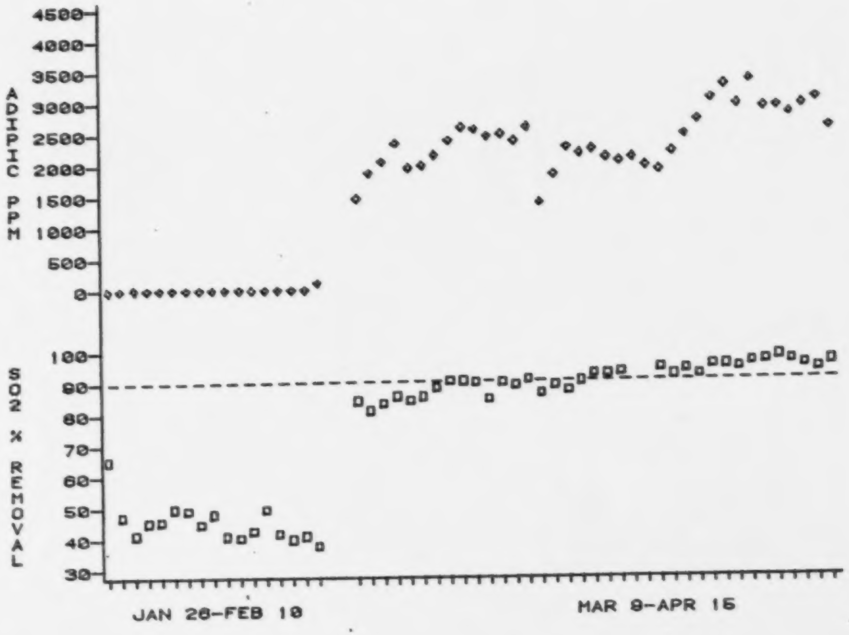
Table 1 gives a summary of important system variables during forced oxidation testing. As the table indicates, several days of testing without TCA spheres was conducted because spheres in Module S-1 were damaged and City Utilities wished to assess the performance of the system without the maintenance prone spheres. The addition of about 1300 to 1500 ppm adipic acid (pH 5.4) increased the SO_2 removal efficiency from below 50 percent to 80-85 percent. The current standard in effect for Southwest Unit 1 is 1.2 lb SO_2/MM Btu (about 82 to 83 percent SO_2 removal depending on fluctuations in coal sulfur content).

Table 1 also shows that Modules S-1 and S-2, operating with about 12 inches of TCA spheres, averaged about 90 percent SO_2 removal with 2300 to 2500 ppm adipic acid compared to below 60 percent SO_2 removal at baseline conditions. S-1 typically achieved slightly lower removal than S-2. This may be attributed in part to slightly higher gas flows and slightly lower slurry flows throughout the testing.

Figures 4 and 5 show the SO_2 removal efficiency as a function of time and adipic acid concentration. Both of these figures indicate improved system performance as the test program progressed. As experience was gained in controlling sulfite blinding and in maintaining a closed water balance, a two week run was made in which both S-1 and S-2 achieved an average SO_2 removal of almost 95 percent. Table 2 gives a breakdown of the SO_2 removal efficiencies during the sustained operating period.

TABLE 1. SUMMARY OF FORCED OXIDATION TESTING

	Operating Time (Hours)	pH	Adipic Acid (ppm)	Atoms O/ Mole SO_2 Removed	SO_2 Removal (%)	Limestone Utilization (%)	Oxidation Efficiency (%)
Testing Without TCA Spheres (Module S-1)							
Baseline (Jan. 10-Feb. 10,1981)	468	5.2	0	3.1	46	89	95
Adipic Acid Addition (Feb. 10-Mar. 1)	135	5.4	1340	2.8	84	89	90
Testing With TCA Spheres							
Baseline - Module S-2 (Jan. 10-Feb. 10)	579	5.4	0	3.0	58	88	91
Adipic Acid Addition - Module S-2 (Feb. 10-Apr. 23)	1168	5.0	2410	3.0	91	92	94
Adipic Acid Addition - Module S-1 (Mar. 1-Apr. 15)	960	5.1	2340	1.3	89	91	74



SCRUBBER MODULE S-1

Figure 4.

SUMMARY OF SPRINGFIELD FORCED OXIDATION/ADIPIC ACID TESTING

SCRUBBER MODULE S-2

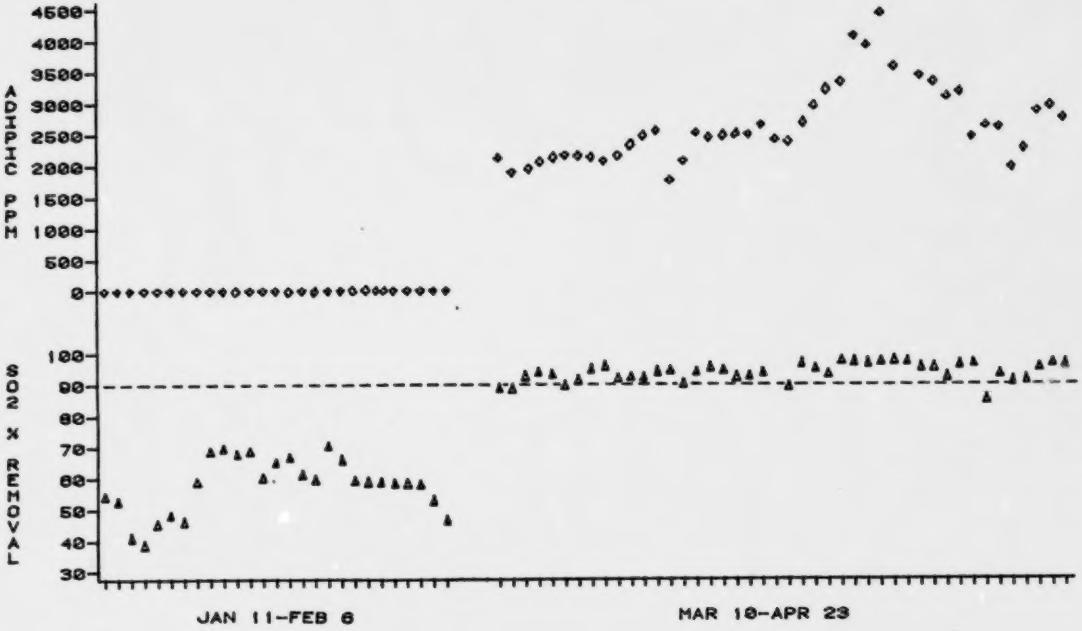


Figure 5.
SUMMARY OF SPRINGFIELD FORCED OXIDATION/ADIPIC ACID TESTING

TABLE 2. DAYS OF OPERATION AT INDICATED SO_2 REMOVAL EFFICIENCY (With TCA Spheres After 3/13/81)

Module	85-90	90-95	95^+
S-1			
(3/13-4/15)	9	15	8
(4/1-4/15)		6	8
S-2			
(3/13-4/23)	3	21	16
(4/1-4/23)	2	5	12

In addition to SO_2 removal, the goals for limestone utilization and sulfite oxidation efficiency were also routinely met. The limestone utilization averaged 88 to 89 percent even for the baseline testing. With adipic acid addition the utilization figure was between 89 and 91 percent. The oxidation efficiency averaged between 90 and 95 percent for S-2 throughout the testing. Compressor malfunctions caused air flows to be reduced in S-1 with a corresponding decrease in oxidation efficiency.

SO_2 Removal

The SO_2 removal efficiencies measured at SWPP were compared with the SO_2 removal correlation developed by Bechtel from the Shawnee results[1]:

$$\text{Fraction } SO_2 \text{ Removal} = 1 - \exp\{-0.0047 \exp(\text{pH} + 0.00062 \text{ Ad})\}$$

where Ad represents the adipic acid concentration of the scrubbing liquor in ppm and pH is that of the scrubber feed slurry. Figure 6 compares the SO_2 removal predicted by the Shawnee correlation with the actual results measured at SWPP. Note that the Shawnee correlation predicts slightly higher removal efficiencies than were routinely achieved at Springfield. This may be because

ADIPIC ACID DEMONSTRATION

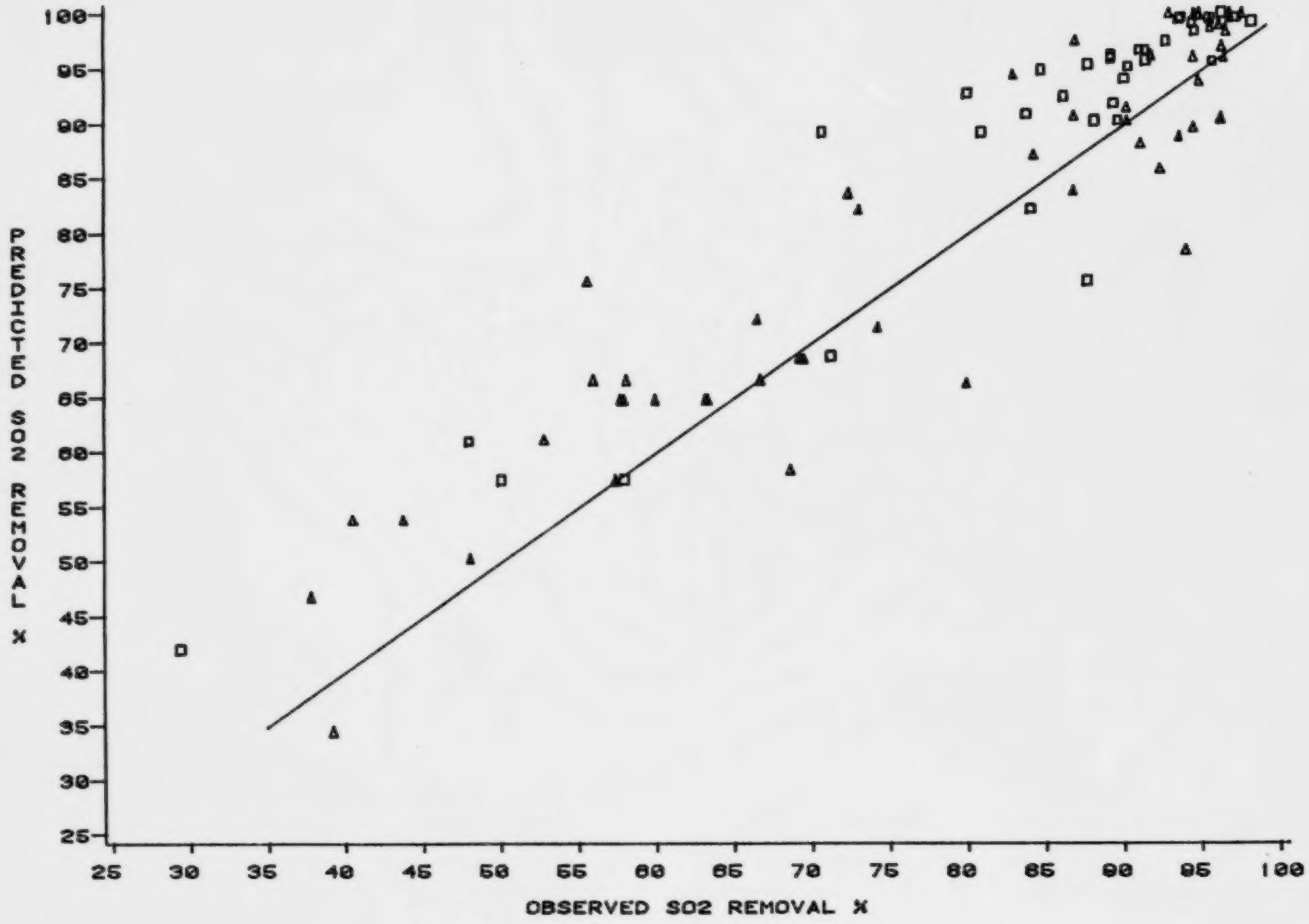


Figure 6

COMPARISON OF PREDICTED AND OBSERVED SO2 REMOVALS
S-1=□ S-2=▲

the level of TCA spheres at Shawnee was 15 inches compared to 12 inches at SWPP. Both the gas and slurry flow rates (on an equivalent cross-sectional area basis) were also lower at Shawnee.

Figures 7 and 8 show the effect of adipic acid concentration on SO_2 removal at scrubber feed pHs of 5.0 and 5.3, respectively. At pH 5.0, the Shawnee correlation predicts 90 percent SO_2 removal at about 1900 ppm adipic acid. The SWPP data indicate that between 2000 and 2500 ppm adipic acid is required. For 95 percent removal, the correlation indicates that 2400 ppm adipic acid would be sufficient while between 2500 and 3000 ppm adipic acid was actually required to routinely achieve that removal level in S-2. Module S-1 did not achieve 95 percent removal until the pH was increased. Figure 8 shows that S-1 achieved 95 percent removal at 5.3 pH and 2700 to 3000 ppm adipic acid.

Overall, the Shawnee correlation predicted the SWPP results fairly closely. These correlations should be quite useful in process design activities as long as some conservatism is used to predict the actual amount of adipic acid required. One positive aspect is that once the process is operating the adipic acid feed rate can be increased to increase the SO_2 removal efficiency. While this increases plant operating cost, a quick response change is available for certain design miscalculations.

There did appear to be a fairly significant difference between the performance of the two modules. S-1 typically showed about two percent lower SO_2 removal efficiency than did S-2. Some of the possible causes include: (1) the liquid feed flow was slightly lower due to the condition of the recycle pumps on S-1 as well as pipe arrangement differences, (2) the gas flow was consistently higher because of mechanical problems with the S-2 fan, and (3) the oxidation efficiency was routinely lower in S-1 than S-2 because of compressor malfunctions. While variations in L/G ratio and oxidation efficiency with each module's data set did not appear to be statistically significant with respect to SO_2 removal efficiency, the operating differences between the two modules could have caused some of the slight differences in SO_2 removal efficiency noted.

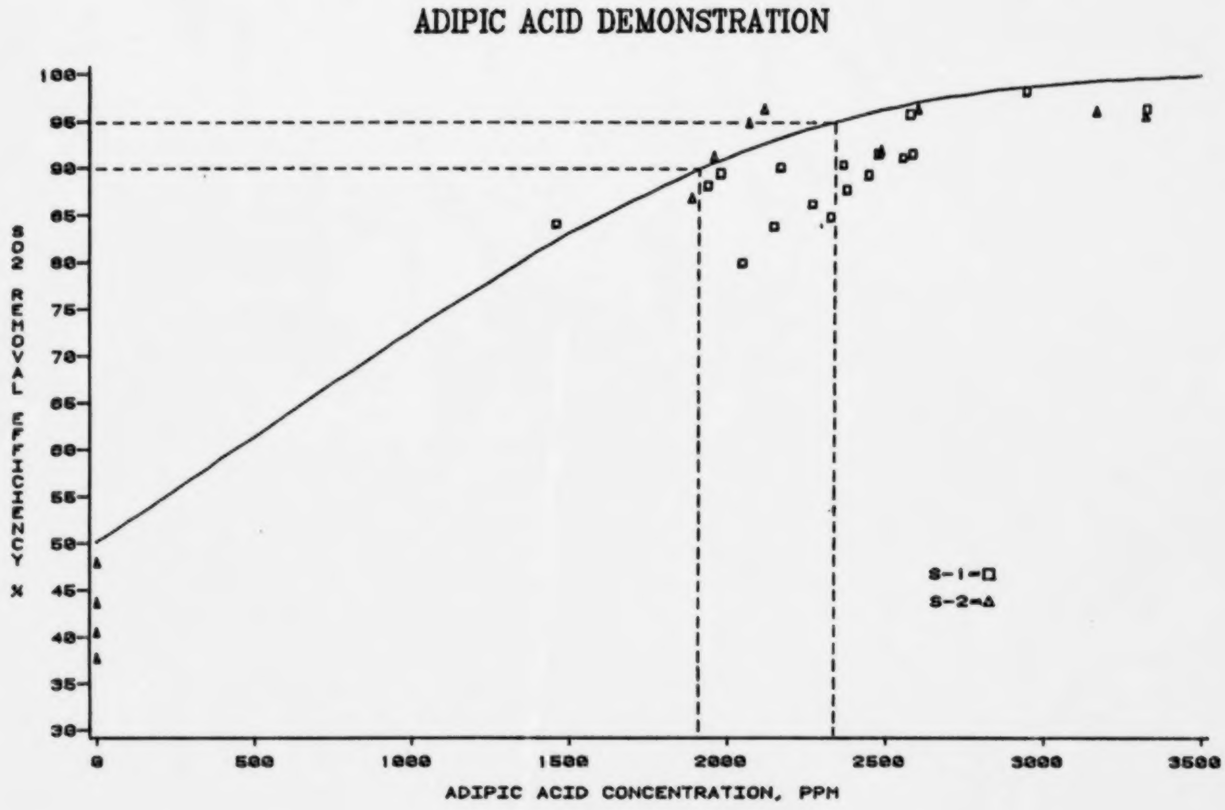

ADIPIC ACID DEMONSTRATION

Figure 7.

FIT OF SPRINGFIELD DATA TO BECHTEL MODEL
SCRUBBER FEED PH=5.0

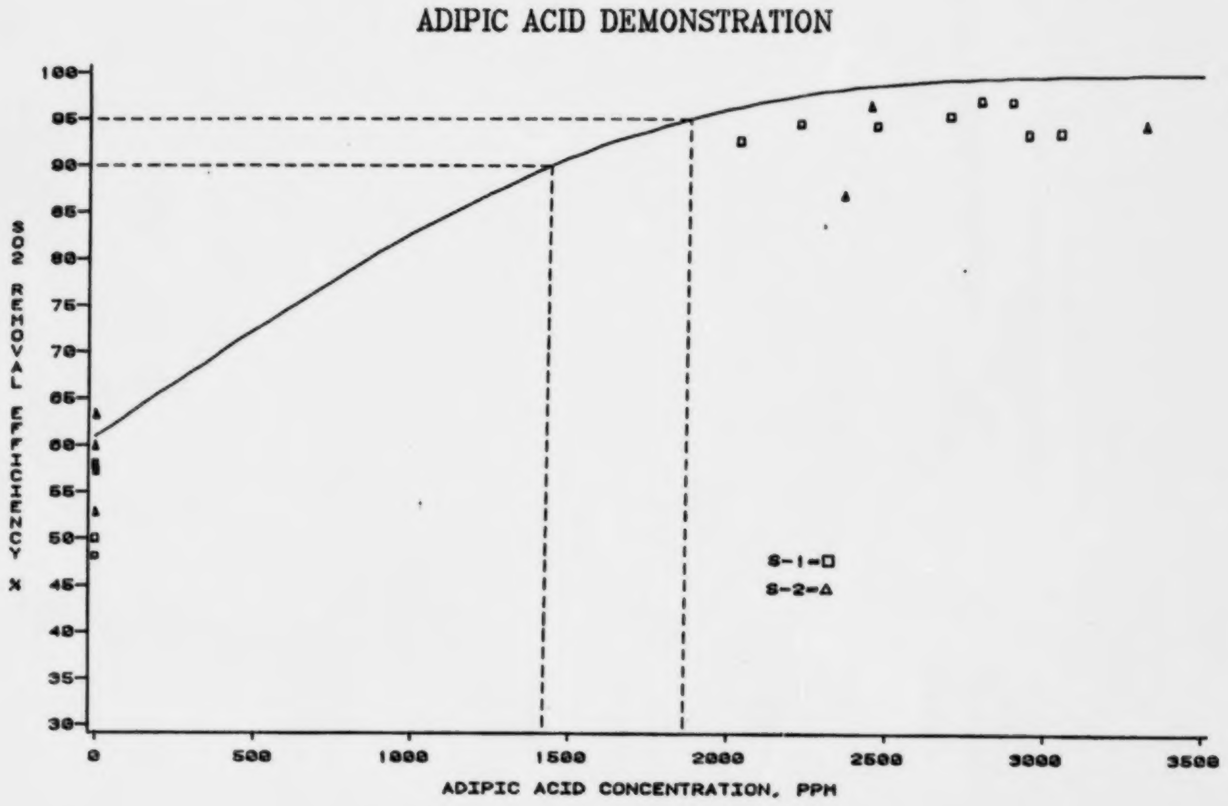


Figure 8.

FIT OF SPRINGFIELD DATA TO BECHTEL MODEL
SCRUBBER FEED PH=5.3

In addition, each of the scrubber modules had several TCA cages which were empty at the end of the forced oxidation testing. The access doors to these cages had come open and the spheres migrated to adjacent cages. Different flow patterns within each module could have also caused the different SO_2 removal efficiency.

The TCA sphere maldistribution certainly could have affected the ability of the scrubber to achieve greater than 95 percent SO_2 removal. An adipic acid concentration change from about 2250 ppm to 3000 ppm resulted in an increase from 90 to 95 percent SO_2 removal in Module S-2 at pH 5.0. Increases in adipic acid concentration above 3000 ppm showed relatively little increase in SO_2 removal. Since the SO_2 removal should not be liquid film limited at above 3000 ppm adipic acid concentration, the relatively constant removal noted with increasing adipic acid concentration is indicative of physical gas-liquid contact limitations.

S-1 was operated for several weeks without TCA spheres to determine the adipic acid level required to achieve about 85 percent SO_2 removal without the maintenance prone spheres. (City Utilities has subsequently replaced the internals in S-1 with trays.) Figure 9 shows the results of this testing. Removals above 80 percent were obtained at 5.4-5.5 pH with about 1500 ppm adipic acid. pHs of 5.8 to 5.9 and 1500 ppm adipic acid resulted in SO_2 removals approaching 90 percent. With an increase in adipic acid concentration to about 2500 ppm and pHs above 5.6, removals above 90 percent were obtained. These high pHs were not maintained for a long period of time, however, so no data were gained concerning scaling potential or long-term scrubber operability.

Limestone Utilization

Table 1 shows that the limestone utilization throughout both the baseline and adipic acid tests averaged above 87 percent. During the adipic acid testing above 90 percent utilization was achieved during periods when sulfite blinding was not a factor. If all the data are considered, the limestone utilization for S-1 drops to about 85 percent while the limestone utilization for S-2 remains

ADIPIC ACID DEMONSTRATION

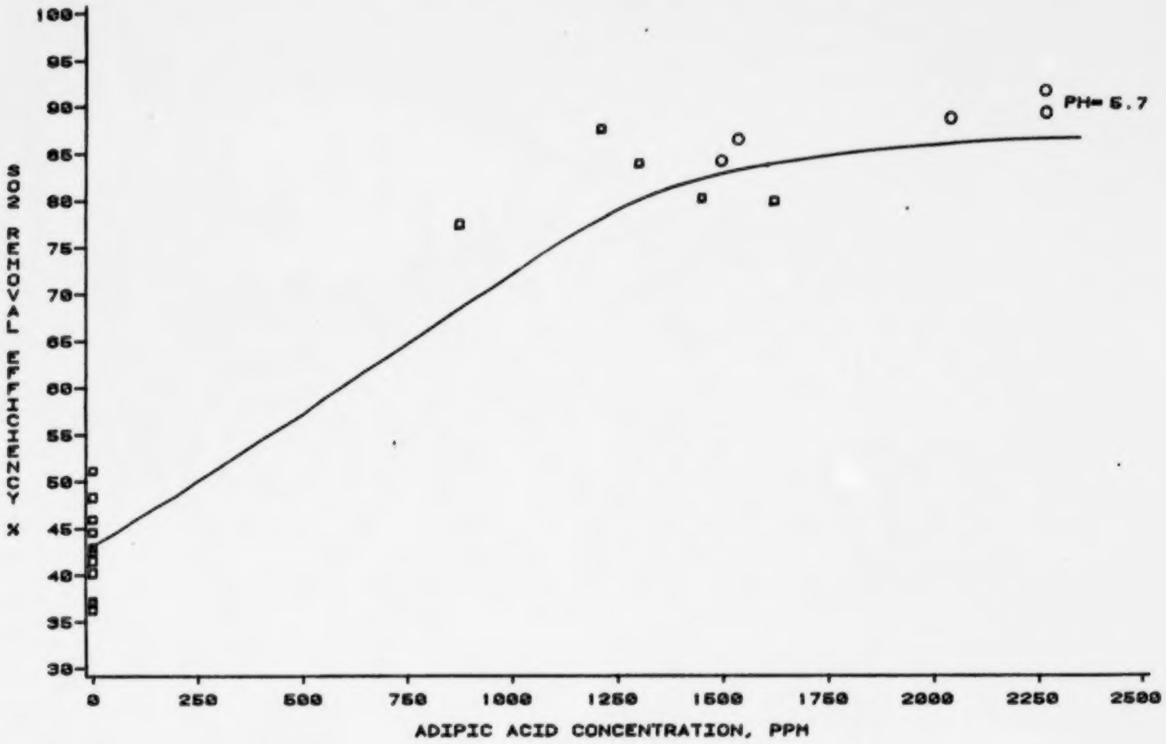


Figure 9.

RESULTS OF TESTING WITHOUT TCA SPHERES
SCRUBBER FEED PH=5.4

above 90 percent. This difference may be due to the fact that higher air rates were used in S-2 which helped that module recover from blinding much more quickly than S-1. The normal operating procedure of sacrificing oxidation in S-1 when compressors malfunctioned limited the available air rate therefore making this module more vulnerable to sulfite blinding.

The major conclusion which can be drawn from the limestone utilization data is that 90 percent utilization can be achieved simultaneously with high SO_2 removal efficiency if adipic acid is used as a buffer. Without adipic acid, higher pHs (and lower limestone utilization) would be required to achieve 90 percent removal. In fact, some other process change in addition to using a higher pH would have to be made to achieve this removal in the scrubbers at Springfield. The baseline forced oxidation tests were not conducted to achieve maximum possible removal efficiencies to limestone utilizations for systems operating with high SO_2 removal efficiencies with and without adipic acid cannot be compared directly.

Sulfite Oxidation

The two primary variables which affected sulfite oxidation were the reaction tank pH and oxidation air rate or O/SO_2 ratio (atoms O/mole SO_2 absorbed). Figure 10 shows the oxidation versus O/SO_2 ratio for two pH ranges. Between 4.9 and 5.1 pH, an O/SO_2 ratio of about 2 yielded above 95 percent oxidation. For pHs above 5.3, an O/SO_2 ratio of about 3 was required for 95 percent oxidation.

Some of the scatter in the data is caused by the pluggage of the air sparger in both scrubbers during the course of the program. During the final forced oxidation inspection at the end of April, less than 10 percent of the sparge holes were clear.

Malfunctions of the air compressors and problems with sulfite blinding required that the S-1 Module be only partially oxidized (about 75 percent oxidation during the adipic acid testing). S-2 was kept fully oxidized as long

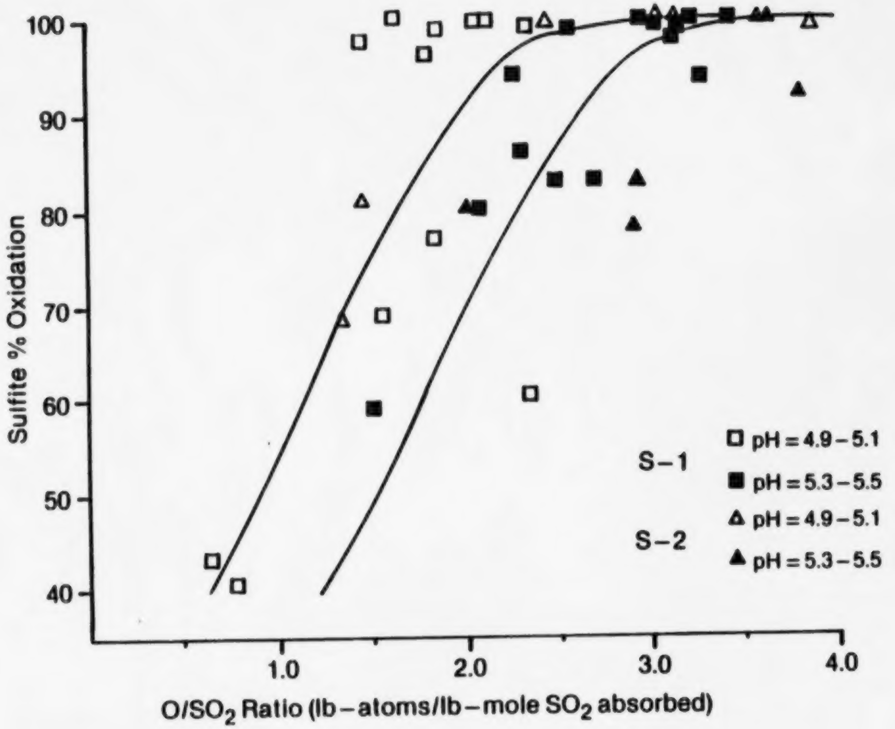


Figure 10.

Effect of pH and O/SO$_2$ Ratio on Sulfite Oxidation Efficiency

as two or more compressors were available for operation. Since all four compressors were required to fully oxidize both modules and oxidation efficiencies of 90 to 95 percent led to frequent episodes of sulfite blinding, it was felt that the most reliable method of operating the scrubbers was full oxidation of S-2 (99+%) and partial oxidation of S-1.

Sulfite Blinding

Sulfite blinding is a phenomenon where high levels of dissolved sulfite react with calcium dissolving from limestone particles to form a calcium sulfite coating on the limestone surface. This coating restricts further limestone dissolution. As a buffer, adipic acid aids in increasing the SO_2 make-per-pass in the scrubber thereby increasing the dissolved sulfite concentration. If the oxidation efficiency is not sufficient and there are not sufficient calcium sulfite seed crystals for precipitation, the sulfite precipitates on the limestone particle effectively inhibiting limestone dissolution. The results of limestone blinding are a drop in the reaction tank pH, an increase in the limestone makeup rate, and a decrease in limestone utilization.

Limestone blinding was not a complete surprise at SWPP since it had been boserved at Shawnee. There were two principal causes of blinding at SWPP: (1) increase in boiler load without accompanying increase in oxidation air, or (2) compressor trips. The boiler load increase early in the morning was the most troublesome. Radian personnel were on site for about 20 hours each day and the early morning load change was made by City Utilities generally prior to 6 a.m. Eventually, instead of optimizing the air rate to each scrubber, the air rate was left at full capacity in S-2 to avoid the blinding.

The initial objective had been to achieve about 95 percent oxidation in each module. However, this level of oxidation did not sufficiently lower the liquor phase sulfite concentration nor did it provide sufficient solid phase calcium sulfite for precipitation seed crystals. Thus, limestone blinding occurred which lowered the pH, SO_2 removal efficiency, and limestone utilization.

There were two mechanisms found to escape blinding. One was to increase the air rate at reduced pH which, in effect, oxidized the sulfite on the limestone surface and alleviated blinding. This was the usual approach with Module S-2. Another approach is to return to the natural oxidation mode of operation which provides sufficient calcium sulfite crystals for sulfite precipitation. Module S-1 was generally operating at below 85 percent oxidation once it became evident that the four compressors could not reliably supply air at a 3.0 O/SO_2 ratio. The second method of elimination seemed to take much longer than the increased oxidation air method. Partial blinding, resulting in sluggish pH control and increased limestone consumption, was also noted and could occur for quite some period before a correction was made. Unless the pH and SO_2 removal dropped suddenly, the reason for increased limestone flows was not as immediately obvious.

Adipic Acid Consumption

Adipic acid may be lost from the system in the liquor associated with the filter cake, in a solid solution or occluded in the solid phase of the filter cake, through fugitive water losses, or by chemical degradation. Table 3 shows the results of adipic acid material balances performed for March and April.

Two sets of adipic acid consumptions are shown. The first is the actual adipic acid added at Springfield while the second number has been corrected for adipic acid accumulation in the system and losses of adipic acid with known fugitive water losses. Even though a concerted effort was made to minimize water losses, an average of about 40 gpm of excess water was fed to the FGD system. In addition, there were other water losses resulting from dewatering plant upsets which were not routed through a water meter. Adipic acid losses associated with these upsets remain in the adjusted adipic acid addition value in Table 3.

The adjusted actual-to-theoretical adipic ratio (defined as adjusted feed rate divided by the adipic acid exiting in the sludge liquor) ranged from 6 during early April to 13 during March. The early April period is significant since major efforts were made at improving dewatering plant operations and decreasing the unmetered losses. The dewatering plant operated well during April 2 to 15 period with no major upsets in spite of the problems created by handling gypsum in a thickener/filter system designed to handle a calcium sulfite sludge.

TABLE 3. ADIPIC ACID MATERIAL BALANCE RESULTS

	March 11-30	April 2-23	April 2-15
Adipic Acid Addition (1000 lbs)	92	59	44
Adjusted Adipic Acid Addition[1] (1000 lbs)	56	38	27
Adipic Acid Losses in Sludge Liquor (1000 lbs)	4.4	6.0	4.7
Actual/Theoretical Ratio[2]	21	10	9
Adjusted Actual/Theoretical Ratio	13	6	6
Adipic Acid Consumption (lb/ton SO_2)	41	31	29
Adjusted Consumption (lb/ton SO_2)	25	20	18
Adjusted Cost (¢/kWh)[3]	0.035	0.027	0.025

[1] The adipic acid addition was reduced by the amount of accumulation plus the adipic lost with fugitive water discharges.

[2] $\text{Actual/Theoretical Adipic Acid Ratio} = \frac{\text{Actual Adipic Acid Added}}{\text{Adipic Acid Lost in Sludge}}$

[3] Assuming Adipic Acid at 60¢/lb.

Perhaps a more useful parameter to consider is the amount of adipic consumed per amount of SO_2 absorbed. During early April, 18 pounds of adipic acid were consumed per ton of SO_2 absorbed. During March the consumption rate was about 40 percent higher. While adipic consumption rates this high were noted at Shawnee on occasion, the adipic acid consumption rates averaged 14 pounds per ton of SO_2 in the runs performed at Shawnee to simulate the Springfield forced oxidation tests.

As far as costs are concerned, the adipic acid added at Springfield would be between 0.025 and 0.035 cents per kilowatt-hour if the known fugitive water losses can be eliminated. This could be even further reduced if the water lost in dewatering could be substantially decreased. These costs do not include any capital expenditures required for an adipic feed system (or to revise dewatering to handle gypsum) nor is there any credit given for possible improvement in reliability due to less changes of scaling and plugging demisters or tower internals.

Equipment Performance

Figure 11 summarizes the hours of operation for the boiler and the two scrubber modules for the baseline test period without adipic addition (January 10 to February 10, 1981) and for the test period with adipic (February 10 to April 23, 1981). As this figure indicates, Module S-1 operated 61 percent of the time the boiler was on-line during the baseline test period. Module S-2 operated 75 percent of the time during the baseline test period. During the adipic testing, Module S-1 operated 65 percent of the time while Module S-2 operated 68 percent of the time. The continuous monitoring system functioned 100 percent of the baseline period and 89 percent of the adipic test period. Much of the downtime during the adipic acid testing occurred in February as a result of damage due to freezing. However, as Figure 12 shows, scrubber reliability was excellent for the majority of the test program.

For the 36 day period March 10 through April 14 Module S-1 was available for all but 10 hours and Module S-2 for all but 7 hours. This represented the best availability achieved up to that time for the FGD system at SWPP. Credit for the notable increases in availability should be given to the combination of overall system improvements both in the mechanics and operation of the scrubbers, and not due solely to the addition of adipic acid. However, operation with adipic acid at fairly low pH (high limestone utilization) and in the forced oxidation mode reduced the chances for calcium solids dissolution in the mist eliminator and TCA cages. Thus, adipic acid should have aided in the higher scrubber system reliability.

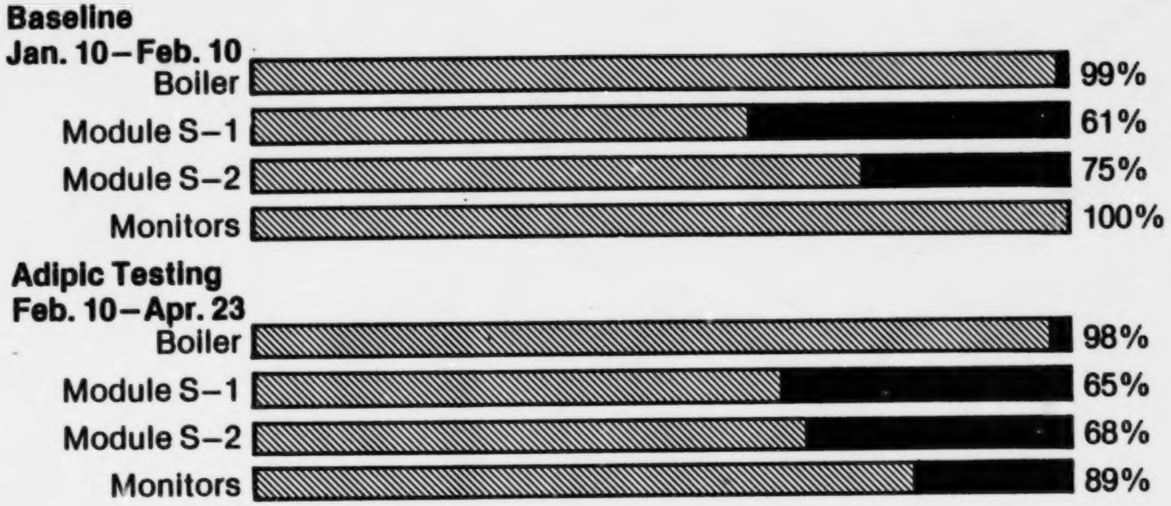


Figure 11.

Boiler, Scrubber, and Continuous Monitor Reliability During Forced Oxidation Testing

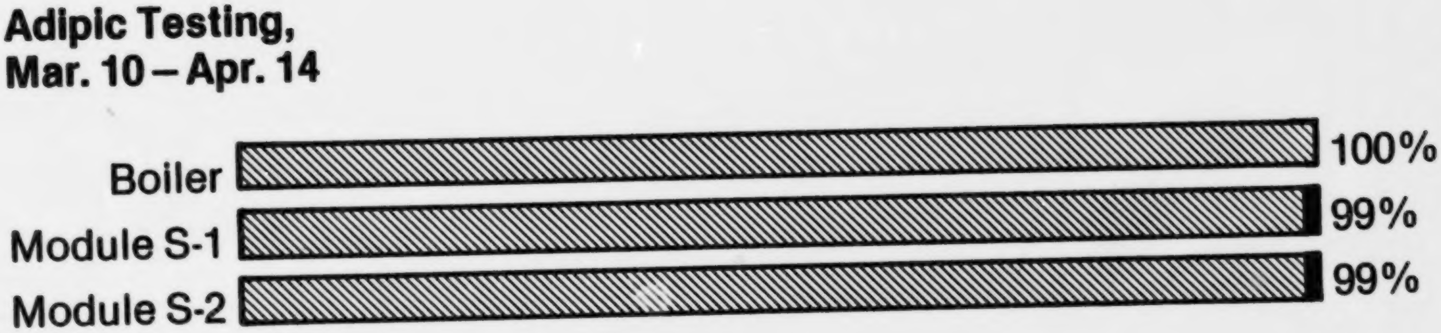


Figure 12.

Boiler and Scrubber Reliability
During March and April (Adipic Acid Testing)

Throughout the test period the condition of the major equipment which made up the FGD system was monitored so that the impact of individual equipment failure on the overall systems availability and performance, especially with respect to SO_2 removal, could be documented. Over the test period there were several equipment failures and malfunctions which limited the system's availability. The following failures/malfunctions accounted for virtually all of the downtime for Module S-1 over the baseline test period:

- A high temperature excursion inside the tower which melted most of the plastic balls.
- Failure of the expansion joint between the A-ID fan and the scrubber module.
- A separation in a water line feeding the module.

Over the adipic test period the following problems were responsible for over 90 percent of Module S-1 downtime.

- Freeze damage to the limestone feed lines, the process water return line from dewatering, and the demister pump and pump suction line.
- Pluggage in the thickener due to sulfate solids.
- Loss of agitator in limestone storage tank.
- A high temperature excursion resulting in melting of the plastic balls.

For Module S-2 most of its downtime during the baseline testing January 10 to February 10 was due to a high temperature excursion which damaged its ball charge. In addition, due to flue gas leaking past the isolation dampers, the module had to be taken off-line several times over a week period to allow maintenance crews to enter S-1 for repair work. During the adipic testing the following problems accounted for most of the forced outages in Module S-2.

- Freeze Damage to return lines from dewatering, demister pump and pump suction line.
- Repair of damage to first level ball cage and the screen and support braces in the presaturator area.
- Damaged limestone feeder belt.
- Pluggage in the thickener due to sulfate solids.
- Loss of agitator in limestone storage tank.

At the beginning and end of each of the test periods the tower sections of each of the scrubber modules were inspected for scale, pluggage, corrosion, and any other damage. Through the entire forced oxidation test period from January to April very little scaling was noticed. The only location within either tower where any scale formation was noticed was on the mist eliminators. This occurred primarily on the upper demisters in each module which are not washed. Scale formation was minor and in only isolated areas in either case. Operation at lower pHs and at high removals for much of the testing helped reduce demister scale formation.

Pluggage of the ball cages in the scrubbers was historically a recurring maintenance problem. This was closely watched for during testing but only a few cages showed signs of pluggage after extended runs. Reasons for this probably include the high loads the system routinely operated at (promoting good turbulence in the cages), reduced ball charges (approximately 12 inches total height), high limestone utilization, and decreased scaling potential due to the presence of calcium sulfate in forced oxidation.

Nozzle damage in the modules was primarily restricted to the presaturator spray nozzles. Most of the nozzles which were made of Carpenter 20 had corrosion damage and in several instances the piping up to the nozzle had corroded away. Improvement in nozzle life had been gained with a piping change in the fall 1980 outage that resulted in supplying clear water to the nozzles instead of solids laden demister wash water. This eliminated errosion damage as well as solids pluggage of these nozzles. No noticeable damage to the ceramic scrubber feed recycle nozzles had occurred. Several of the nozzles had plugged either partially or completely in each module with pieces of rubber liner and plastic balls, but this problem was not widespread.

The high temperature excursions that caused forced outages during the testing were the result of a loss of power to the pumps which supply the quench water to the presaturator. Without this water hot flue gas (300°F) enters the towers, melting the plastic balls. The emergency scrubber trip goes into effect when high temperatures are measured in the presaturator, but the flue gas cannot be isolated from the towers instantaneously since the dampers normally require one or two minutes to close. A source of quench water was later piped to the presaturator from the plant fire water system which should eliminate this problem in the future.

Numerous problems were encountered with the equipment on the sludge dewatering plant during the testing. These problems were the result primarily of the faster settling calcium sulfate solids. The plant was originally designed for dewatering a slurry that was primarily calcium sulfite. Pluggage was routine at a number of points around the dewatering plant. Normally this resulted in discharges of slurry from the system to clear the pluggage. At one time the pluggage was severe enough to require draining and cleaning the thickener, which brought the two scrubber modules offline.

Maintaining consistent and accurate operation of the on-line plant pH meters was very difficult. Calibration was required every 24 hours at a minimum. Signal drift and erratic response were almost daily occurrences. Most of the problem appeared to be due to the wet environment on top of the reaction tanks where the instruments were located. There was significant quantities of air sparged into the reaction tanks for forced oxidation which escaped the top of the tanks saturated with water. The cold weather caused the moisture to condense on the pH instrumentation in spite of the weather protection enclosure. Several times both primary and backup pH electrodes malfunctioned. During these periods, manual readings by Radian would be used to keep the module operating as close to the set point as possible. As the weather warmed through the testing the problems became much less frequent. Daily calibration of the meters was continued to minimize span drift.

Freeze damage to the piping around the FGD system was due to the ineffectiveness of heat tracing the original FRP piping. Much of this pipe has been replaced with rubber lined carbon steel pipe which was heat traced and insulated. As a result through the winter months only a small number of freeze failures were experienced and only one resulted in a major forced outage.

Over the course of the forced oxidation test period the continuous monitoring system was available and operating for 96 of the 104 days. The majority (5 days) of the downtime was due to a relay coil failing in the circuitry that controls the switching of the analyzers from one module to the other. The analyzers and data acquisition system were inspected several times daily. Close tracking of their operation helped reduce monitoring system downtime by early detection of problems. Corrective measures could then be taken often before data quality was affected.

City Utilities has maintained a continuing effort to improve the overall equipment performance of the SWPP scrubbers. Since the beginning of the on-site phase of the adipic demonstration test program in late July, 1980, numerous changes have been made, including those described above, which have increased the reliability and operability of the FGD system. Table 4 summarizes most of the improvements which have been made in the last year. Many had been completed by the start of the forced oxidation testing. Other changes took place during the testing. The combination of these revisions was partly responsible for the notable improvement on system reliability during March and April. In addition, the forced oxidation/adipic acid test conditions contributed to the improved reliability by reducing mist eliminator and TCA liquor scaling potential.

TABLE 4. SUMMARY OF CHANGES TO IMPROVE SYSTEM RELIABILITY

- Replaced FRP (plastic) pipe with lined steel pipe for added strength and improved heat tracing for freeze protection.
- Used clear liquor for cooling the flue gas in the presaturator.
- Revised the limestone feed loop to include an automatic water flush to remove limestone slurry when flow stopped.
- Made several changes in the dewatering plant including (1) 24 hour operation and maintenance, (2) larger drive motor for the pug mill that mixes the filter cake and fly ash, and (3) installed a separate return line to the thickener for the filtrate.
- Replaced inlet isolation damper drive motors with larger ones.
- Reduced the on-off cycling of the scrubbers by cooperative system load management.
- Decreased the ball charge in the two towers.
- Replaced the ball cages in Module S-1 with three perforated stainless steel trays.

During the three week maintenance outage that began at the end of the forced oxidation testing in April, Module S-1 was converted to a tray tower. This change was made not only to decrease the maintenance associated with operating a TCA but also to investigate it as a means of improving SO_2 removal.

REFERENCE

1. Burbank, D.A. and S.C. Wang. "Test Results on Adipic Acid-Enhanced Lime/Limestone Scrubbing at the EPA Shawnee Test Facility", presented at the EPA Lime/Limestone Industry Briefing, December 5, 1979, Raleigh, North Carolina.

EVALUATION OF THE ADIPIC ACID ENHANCED LIMESTONE FLUE GAS DESULFURIZATION PROCESS ON AN INDUSTRIAL BOILER

Prepared by:

R. W. Gerstle and D. S. Henzel
PEDCo Environmental, Inc.
11499 Chester Road
Cincinnati, OH 45246

and

J. David Mobley
Industrial Environmental Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

EPA Contract No. 68-02-3173, Task 39

Presented at:

EPA's Industry Briefing on the
Adipic Acid Enhanced Limestone FGD Process

Springfield, MO
July 15, 1981

Preceding page blank

EVALUATION OF THE ADIPIC ACID ENHANCED LIMESTONE FLUE GAS DESULFURIZATION PROCESS ON AN INDUSTRIAL BOILER

ABSTRACT

The purpose of this study was to evaluate the effect of the addition of adipic acid on the SO_2 removal of a wet limestone flue gas desulfurization (FGD) system on a coal-fired industrial boiler facility. The boiler facility at the Rickenbacker Air National Guard Base near Columbus, Ohio, was selected for this study. Emission data were collected in accordance with the promulgated regulations for SO_2 compliance data as specified in the Federal Register. The test results show that the addition of adipic acid to the limestone slurry significantly improved the SO_2 removal efficiency of the FGD system. Limited baseline data on operations with limestone only indicated a performance level of 55 percent SO_2 removal. With the addition of about 2200 ppm of adipic acid to the limestone scrubbing system, the unit's level of performance increased to an average of 94.3 percent SO_2 removal over a 30-day test period.

EVALUATION OF THE ADIPIC ACID ENHANCED LIMESTONE FLUE GAS DESULFURIZATION PROCESS ON AN INDUSTRIAL BOILER

INTRODUCTION

This report describes how the addition of adipic acid to a wet limestone scrubber system affects sulfur dioxide (SO_2) removal efficiency. The site selected for the test, Rickenbacker Air National Guard Base (RANGB) near Columbus, Ohio, has six spreader stoker boilers with a total capacity of 222 GJ/h (210×10^6 Btu/h). The boilers produce hot water, primarily for space heating. Sulfur dioxide emissions are controlled by a scrubber system manufactured by Research-Cottrell under license from A. B. Bahco of Sweden. The FGD system, as shown in Figure 1, consists of a mechanical collector, Swedish Bahco scrubber tower, limestone storage and handling system, clarifier (thickener), booster fan, sludge disposal pond, and associated ductwork, pumps, and controls. Table 1 presents key design parameters for the scrubbing system. During the test a mechanical dry feeder introduced the adipic acid into the scrubber system at the same location where fresh limestone is added.

Untreated flue gas from the individual boilers enters a common header equipped with a bypass stack and is fed through a mechanical collector for primary removal of particulates. The design removal efficiency of the mechanical collector is 70 percent. A fan then introduces the partially cleaned flue gas into the scrubbing tower for SO_2 removal.

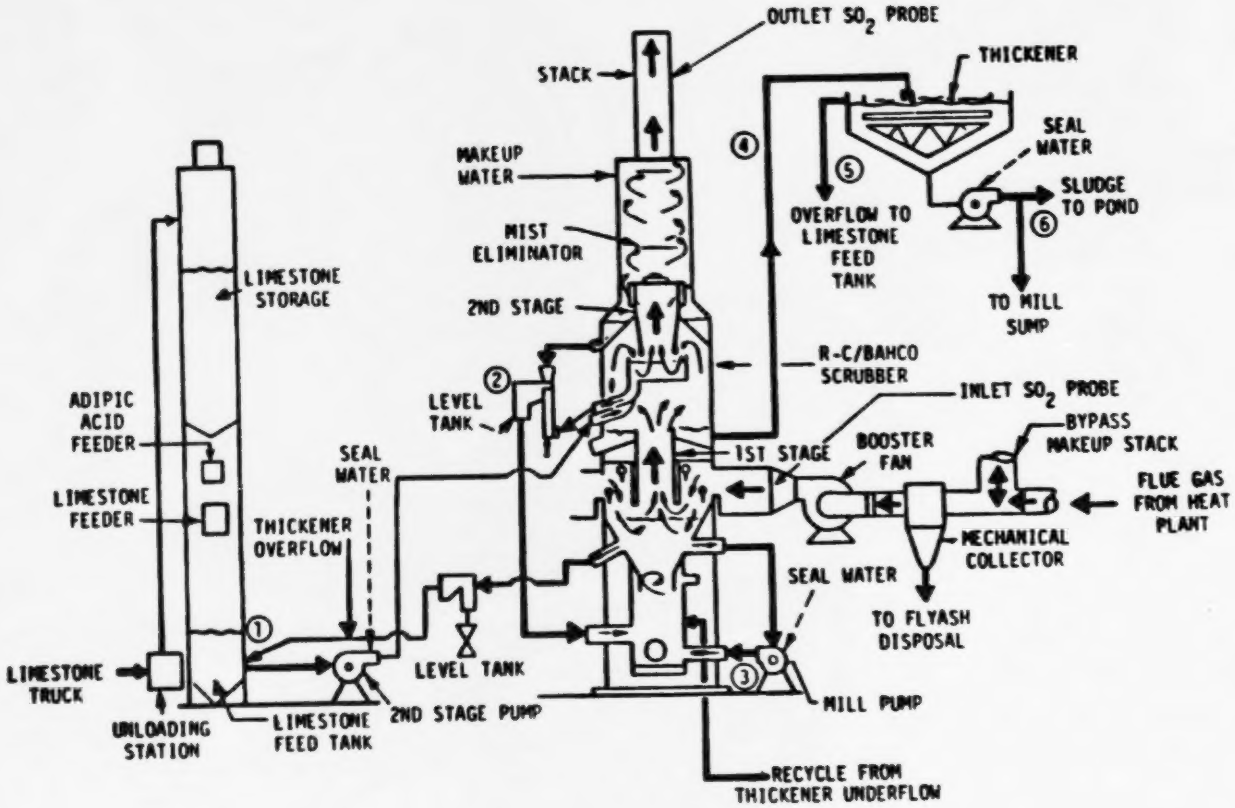

OUTLET SO_2 PROBE
STACK
THICKENER
MAKEUP WATER
④
SEAL WATER
⑤
SLUDGE TO POND
⑥
MIST ELIMINATOR
OVERFLOW TO LIMESTONE FEED TANK
LIMESTONE STORAGE
TO MILL SUMP
2ND STAGE
R-C/BAHCO SCRUBBER
②
INLET SO_2 PROBE
ADIPIC ACID FEEDER
LEVEL TANK
BYPASS MAKEUP STACK
1ST STAGE
BOOSTER FAN
SEAL WATER
FLUE GAS FROM HEAT PLANT
LIMESTONE FEEDER
MECHANICAL COLLECTOR
THICKENER OVERFLOW
SEAL WATER
①
TO FLYASH DISPOSAL
LIMESTONE TRUCK
LEVEL TANK
③
UNLOADING STATION
LIMESTONE FEED TANK
2ND STAGE PUMP
MILL PUMP
RECYCLE FROM THICKENER UNDERFLOW

Figure 1. Flow diagram of the scrubber system at Rickenbacker.

TABLE 1. DESIGN PROCESS INFORMATION FOR RICKENBACKER AIR NATIONAL GUARD BASE SCRUBBING SYSTEM

Total rating	2600 Nm^3/s (55,000 scfm)
Number of boilers	6
Boiler capacity	222 GJ/h (210 x 10^6 Btu/h)
Number of separate FGD units	1
Control system vendor	Research-Cottrell/Bahco
Type of FGD system	Retrofit
Startup date	March 1976
SO_2 removal efficiencies	90%+ design with lime operation; lower with limestone operation
Particulate removal efficiency	98% design
Water makeup	Open loop
Sludge or byproduct disposal	Unstabilized $CaSO_3/SO_4$ sludge to lined pond

The Bahco scrubber is a vertical tower consisting of two inverted venturi scrubbing stages. When the untreated gas enters the first stage, it is diverted downward to impinge on the liquid slurry surface of the mill. The gas then rises through the first stage venturi, where it intimately mixes with the slurry droplets now entrained in it. The partially scrubbed gas is then diverted downward onto the liquid slurry surface in the second-stage pan, and the process is repeated. The treated gas is then directed upward into a cyclonic mist eliminator, where entrained slurry droplets are removed before the gas exits through a stub stack to the atmosphere.

A certified extractive continuous emission monitor (CEM) system and an onsite computer measured and recorded concentrations of SO_2 and O_2 in the flue gas stream. Equipment at RANGB includes a continous SO_2 monitoring system on the scrubber, which was used during the test after some maintenance work and calibration. Research Triangle Institute, under contract to EPA, audited the monitoring system on March 5 and 6, 1981, and found it to be operating properly.

Both the certification (based on Federal Register procedures) and internal audits (based on certified SO_2 and O_2 gases) showed that the monitors were operating properly. Some problems entailing unscheduled maintenance were encountered during the initial 168-hour monitor conditioning period. Also, on March 20 a small leak was discovered in the SO_2 monitor internal valving system. Apparently, rich inlet gas had leaked through this valve into the outlet gas sample stream, which caused a slightly higher outlet SO_2 concentration reading and a correspondingly lower calculated SO_2 removal efficiency. The extent of the leak was determined by introducing audit gases and making manual SO_2 tests of the flue gases, and a correction factor was applied to the outlet readings from March 18 until the leak was repaired on April 3.

TEST PROCEDURE

The adipic acid test period at RANGB was from February 9 to April 10, 1981, during which time the necessary equipment was set up and calibrated and data were collected. The monitoring equipment began operating on February 13, but the first few weeks of the test were used for shakedown and calibration of the monitors. The data collected included measured SO_2 and O_2 concentrations in the gas stream at the scrubber inlet and outlet and chemical analyses of the scrubber slurry, limestone, and coal. Scrubber and boiler operating conditions were recorded several times daily.

The adipic acid feeder was set up for continuous addition of the adipic acid to the slaker--the same location at which fresh limestone is added. When large quantities were necessary to increase slurry concentrations, the adipic acid was manually introduced directly into the thickener tank because the sudden addition of adipic acid in large quantities to the slaker caused foaming in the slurry. This did not occur in the thickener.

Slurry analyses were performed at the site, but periodic samples were checked at the base laboratory for quality control. The adipic acid analytical procedure utilized silicic acid and provided the concentration of all carboxylic acids, not just adipic. As indicated by the numbers in Figure 1, liquid samples were taken at (1) the limestone slurry feed into the scrubber, (2) the second-stage level tank, (3) the mill recycle loop (known as the mill pump sample), (4) the thickener inlet stream, (5) the thickener overflow, and (6) the thickener underflow stream. Because the limestone slurry feed sample was used as a control sample, it was taken twice a day. The mill pump sample was taken once a day, and samples were taken from all six locations once a week. Slurry solid samples, taken by filtering samples from the liquid sample streams, included the limestone slurry feed (once a week), the thickener inlet (three times a week), and the thickener underflow (once a week, usually while sludge was being pumped to the settling pond). Coal samples were taken once a day, and limestone samples were taken once a week. The coal samples were combined into weekly composites before being analyzed.

For achievement of the highest SO_2 removal efficiency, the best limestone utilization and the most efficient use of adipic acid, optimum scrubber operation was maintained by keeping the pH of the limestone dissolver tank slurry near 5.0. This was done by manually adjusting the limestone feed rate as necessary to correspond with changes in the boiler load. Except during occasional upsets in scrubber operations, the adipic acid feed rate remained constant at a concentration of 2000 to 2500 ppm throughout the test. On March 20 and 21 the limestone feed rate and adipic acid concentrations were increased in an effort to achieve still higher SO_2 removal efficiency.

From March 4 to April 10 the test was interrupted only twice because of scrubber operation. On March 23 the electrical power to the scrubber was interrupted, and on March 30 the scrubber was shut down because the thickener tank had plugged, apparently as the result of some plastic sheeting, and remained down until about 8:00 a.m. on April 1. On April 10 the addition of adipic acid was stopped and the continuous monitoring program was terminated. Sufficient data had been accumulated by that time, and warmer weather was resulting in increasingly reduced boiler loads.

QUALITY ASSURANCE PLAN FOR CONTINUOUS MONITORING

PEDCo performed a quality assurance check on the continuous emission monitoring system (CEMS) to ensure the reliability of the data collected.

The check consisted of two distinct but equal functions: (1) the assessment of the quality of the CEMS data through estimation of precision and accuracy, and (2) the control and improvement of the quality of the CEMS data through implementation of quality control policies and corrective actions. The second function was related to the first in that determination of data quality inadequacy resulted in an increase in the quality control effort until the data were considered acceptable.

The field operations included standard daily procedures for ensuring that the following activities were performed adequately.

Calibration of the CEMS

The CEMS was calibrated by use of gases with known SO_2 concentrations. Two gases and ambient air were run through the analyzer for each testing mode (inlet and outlet). The results of each were recorded, and any necessary adjustments were made.

All activities involved in routine calibration and adjustment of the CEMS were recorded daily in a standard calibration data log.

Calibration of Drift Determination

Daily initial calibration readings for all CEMS zero and span values were compared with the final calibration readings of the preceding day to determine if any change had occurred in 24 hours. Seven consecutive sets of these initial/final readings were recorded for each parameter to determine 24-hour drift.

Preventive Maintenance for CEMS

The CEMS was regularly inspected to ascertain problems that might lead to loss in operability or data quality. Each day the four separate systems of the CEMS were checked independently: the SO_2 analyzer, the O_2 analyzer, the instrument recorders, and the sampling interface.

Program of Corrective Action for Malfunctioning CEMS

Any possible CEMS malfunctions that came to light during preventive maintenance checks prompted immediate corrective action. A complete log of all CEMS malfunctions and corrective actions was maintained.

Accuracy Assessment

PEDCo performed relative accuracy tests on the continuous emission monitoring system according to EPA reference methods and system audits with EPA-tested audit gases based on Standard Reference Materials (SRM).

Figures 2 and 3 show the locations of the continuous monitor probes and reference method sampling ports for the inlet and outlet. Inlet and outlet sampling locations were selected to be representative of the streams tested and to achieve equivalence between manual and CEMS samples.

Performance Specification Test Regulations require that a minimum of 9 and a maximum of 12 sets of reference method data be taken at a rate of no more than one set per hour. Regulations also require that the analyzer monitor stack gas concentrations continuously during reference method testing.

All data derived by use of the reference method and the continuous monitor are presented on a dry basis, and a moisture correction factor is used to present results on a consistent basis. Sulfur dioxide and oxygen tests were run simultaneously. The CEM analysis of moisture content was determined by measuring the temperature of a sample taken after the moisture trap in the sampling system. Moisture content was then calculated because the gas stream being analyzed was saturated.

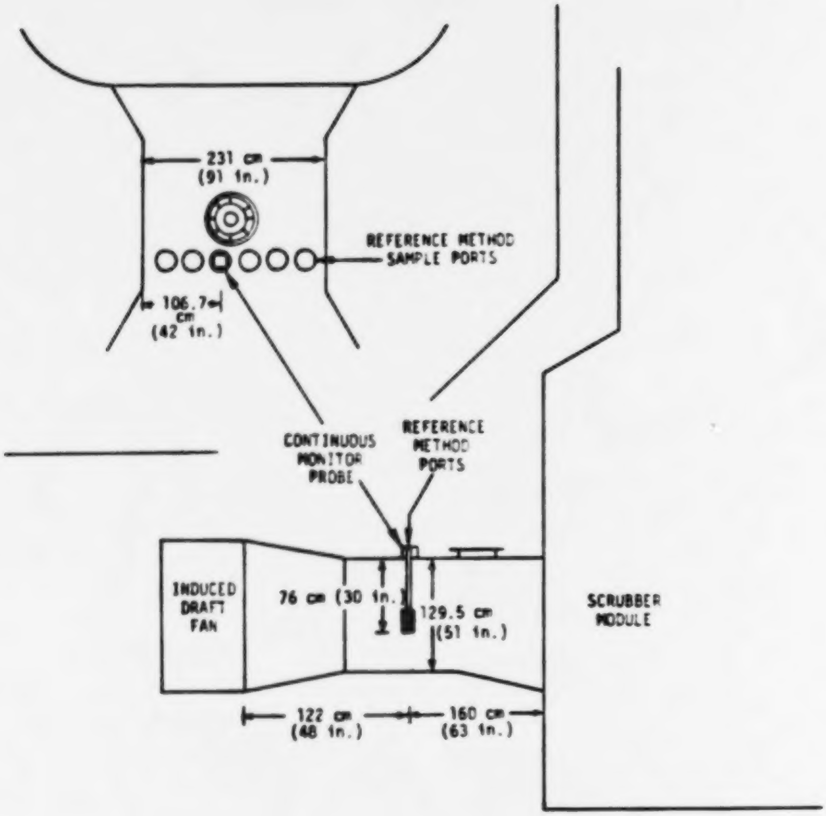

231 cm
(91 in.)
REFERENCE METHOD
SAMPLE PORTS
106.7 cm
(42 in.)
CONTINUOUS
MONITOR
PROBE
REFERENCE
METHOD
PORTS
INDUCED
DRAFT
FAN
76 cm (30 in.)
129.5 cm
(51 in.)
SCRUBBER
MODULE
122 cm
(48 in.)
160 cm
(63 in.)

Figure 2. Scrubber inlet sampling locations.

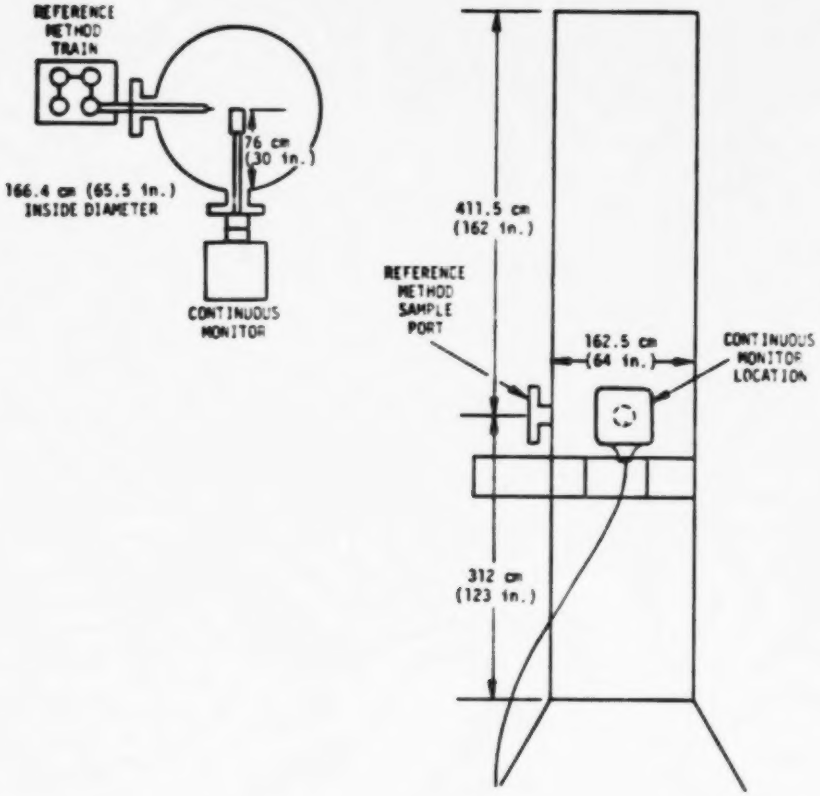

REFERENCE METHOD TRAIN
76 cm (30 in.)
166.4 cm (65.5 in.) INSIDE DIAMETER
CONTINUOUS MONITOR
411.5 cm (162 in.)
REFERENCE METHOD SAMPLE PORT
162.5 cm (64 in.)
CONTINUOUS MONITOR LOCATION
312 cm (123 in.)

Figure 3. Scrubber outlet sampling locations.

Tables 2 and 3 present the relative accuracy data for the initial certification period. Relative accuracy calculations based on nine sets of reference method data were performed according to equations in Section 7, Appendix B, Federal Register, Vol. 44, No. 197. These calculations showed that the relative accuracy at the inlet was 1.72 percent based on SO_2 concentrations and 7.30 percent when the SO_2 was expressed on a weight per heat input basis. The corresponding values at the scrubber outlet were 18.67 and 16.43 percent, respectively.

Performance Audits

Performance audits were conducted to maintain quality control throughout the monitoring period. Audit gases certified by the EPA were introduced at the scrubber inlet through a manifold pressurized to 3.39 kPa (1 in. Hg) to duplicate sampling conditions. Audit gases were introduced at the scrubber outlet through an open-end manifold at ambient atmospheric pressure. No adjustments were made to the analyzer flow rates. Analyzer response to audit concentrations was determined by the computer used for storage and retrieval of the emission monitoring data. Results of these tests showed excellent agreement between the audit gas concentrations and analyzer readings for SO_2 and oxygen at both the inlet and outlet sites.

RESULTS

Table 4 summarizes the daily average SO_2 monitoring data for those 30 days when 18 hours or more of acceptable readings were obtained and high efficiency was achieved. These data show that 94.3 percent was the mean SO_2 removal efficiency achieved, with a corresponding standard deviation of 2.1. These data do not include days when the limestone feed rate was low or when other known operating problems occurred. The emission values are based on

TABLE 2. INLET REFERENCE METHOD AND CEM RESULTS

Test No.	Time	Reference method								Monitor[a]			
		Vm[b] (std)		g/Nm^3	(10^{-4} lb/dscf)	SO_2, ppm	ng/J	(lb SO_2/ 10^6 Btu)	% O_2	SO_2, ppm	ng/J	(lb SO_2/ 10^6 Btu)	% O_2
		Nm^3	(dscf)										
RIC-1	0749-0819	0.0251	(0.888)	2.03	(1.27)	775	1965.1	(4.57)	15.2	753	1930.7	(4.49)	14.9
RIC-2	0926-0951	0.0257	(0.908)	2.15	(1.34)	816	1849.0	(4.30)	14.5	803	2132.8	(4.96)	15.1
RIC-3	1010-1035	0.0254	(0.897)	2.11	(1.32)	802	1849.0	(4.28)	14.6	805	2029.6	(4.72)	14.8
RIC-4	1110-1135	0.0257	(0.908)	1.94	(1.21)	734	1840.4	(4.28)	15.1	736	1887.7	(4.39)	14.9
RIC-5	1210-1235	0.0254	(0.896)	1.76	(1.10)	671	1831.8	(4.26)	15.6	668	1711.4	(3.98)	14.9
RIC-6	1310-1335	0.0274	(0.967)	2.02	(1.26)	766	1763.0	(4.10)	14.6	793	1874.8	(4.36)	14.4
RIC-7	1410-1435	0.0277	(0.979)	1.92	(1.20)	753	1737.2	(4.04)	14.6	768	1874.8	(4.36)	14.6
RIC-8	1510-1535	0.0265	(0.937)	1.83	(1.14)	693	1732.9	(4.03)	15.1	694	1874.8	(4.36)	15.2
RIC-9	1610-1635	0.0278	(0.982)	1.83	(1.14)	697	1732.9	(4.03)	15.1	689	1797.4	(4.18)	15.0
RIC-10	1710-1735	0.0286	(1.01)	1.86	(1.16)	703	1775.9	(4.13)	15.1	707	1724.3	(4.01)	14.6

[a] Three monitor readings taken during reference method run. Monitor readings were then averaged for final emission results.

[b] Vm = metered volume (dry basis).

TABLE 3. OUTLET REFERENCE METHOD AND CEM RESULTS

Test No.	Time	Reference method[a]								Monitor			
		Vm^b (std) Nm³	Vm^b (std) (dscf)	g/Nm³	(10^{-4} lb/dscf)	SO_2, ppm	ng/J	(lb SO_2/10^6 Btu)	% O_2	SO_2, ppm	ng/J	(lb SO_2/10^6 Btu)	% O_2
ROC-1	0832-0857	0.0270	(0.952)	0.072	(0.045)	27.4	63.2	(0.147)	14.6	26.6	56.7	(0.132)	13.7
ROC-2	0952-1017	0.0266	(0.941)	0.051	(0.032)	19.2	43.4	(0.101)	14.4	39.2	72.6	(0.169)	12.6
ROC-3	1052-1117	0.0263	(0.930)	0.091	(0.057)	34.5	78.6	(0.183)	14.5	40.2	103.6	(0.241)	12.8
ROC-4	1202-1227	0.0286	(1.01)	0.062	(0.039)	23.7	54.6	(0.127)	14.5	29.0	78.2	(0.182)	15.2
ROC-5	1302-1327	0.0284	(1.002)	0.061	(0.038)	23.2	52.4	(0.122)	14.5	29.2	61.5	(0.143)	13.6
ROC-6	1412-1437	0.0275	(0.972)	0.087	(0.054)	32.8	67.9	(0.158)	13.9	33.1	67.0	(0.156)	13.3
ROC-7	1512-1537	0.0278	(0.982)	0.075	(0.047)	29.2	64.5	(0.150)	14.2	35.3	83.8	(0.195)	12.7
ROC-8	1612-1637	0.0323	(1.14)	0.067	(0.042)	25.6	55.4	(0.129)	14.2	34.1	64.5	(0.150)	12.8
ROC-9	1717-1742	0.0289	(1.022)	0.062	(0.039)	24.0	57.2	(0.133)	14.9	20.1	44.3	(0.103)	13.9
ROC-10	1807-1832	0.0296	(1.046)	0.088	(0.055)	33.6	80.8	(0.188)	14.9	36.3	71.3	(0.166)	13.1
ROC-11	1907-1932	0.0298	(1.053)	0.095	(0.059)	36.2	82.5	(0.192)	14.6	34.6	81.7	(0.190)	14.4
ROC-12	2007-2032	0.0276	(0.973)	0.088	(0.055)	33.7	68.8	(0.160)	13.9	37.4	83.4	(0.194)	14.0

[a] Emission results based on use of 0.001 N barium perchlorate.

[b] Vm = metered volume (dry basis).

TABLE 4. 30-DAY SUMMARY OF SO_2 CONCENTRATIONS AND SCRUBBER EFFICIENCY MARCH-APRIL 1981

DATE	# HOURS CEM DATA	SO2 INLET LB/MMBTU	SO2 INLET NG/J	SO2 OUTLET LB/MMBTU	SO2 OUTLET NG/J	EFF %
MARCH 4	24	4.00	1719.8	0.30	129.0	92.5
MARCH 5	18	3.10	1332.9	0.14	60.2	95.5
MARCH 6	21	4.11	1767.1	0.24	103.2	94.2
MARCH 7	23	3.82	1642.4	0.30	129.0	92.1
MARCH 8	19	4.16	1788.6	0.37	159.1	91.1
MARCH 9	20	4.17	1792.9	0.27	116.1	93.5
MARCH 10	20	4.88	2098.2	0.27	116.1	94.5
MARCH 11	19	4.37	1878.9	0.21	90.3	95.2
MARCH 12	18	4.45	1913.3	0.22	94.6	95.1
MARCH 14	18	6.19	2661.4	0.45	193.5	92.7
MARCH 15	22	5.21	2240.1	0.30	129.0	94.2
MARCH 20	21	4.95	2128.3	0.32	137.6	93.5
MARCH 21	19	5.22	2244.4	0.15	64.5	97.1
MARCH 22	23	4.64	1995.0	0.25	107.5	94.6
MARCH 24	22	5.48	2356.1	0.55	236.5	90.0
MARCH 25	18	4.97	2136.9	0.32	137.6	93.6
MARCH 26	21	6.15	2644.2	0.32	137.6	94.8
MARCH 27	21	4.85	2085.3	0.29	124.7	94.0
MARCH 28	23	4.52	1943.4	0.43	184.9	90.5
MARCH 29	19	6.43	2764.6	0.61	262.3	90.5
MARCH 30	18	5.38	2313.1	0.36	154.8	93.3
APRIL 2	24	4.83	2076.7	0.14	60.2	97.1
APRIL 3	21	5.07	2179.9	0.13	55.9	97.4
APRIL 4	22	4.79	2059.5	0.18	77.4	96.2
APRIL 5	22	5.27	2265.9	0.33	141.9	93.7
APRIL 6	22	5.15	2214.3	0.19	81.7	96.3
APRIL 7	22	5.40	2321.7	0.17	73.1	96.9
APRIL 8	23	5.50	2364.7	0.21	90.3	96.2
APRIL 9	22	6.16	2648.5	0.34	146.2	94.5
APRIL 10	23	5.06	2175.6	0.16	68.8	96.8
MEAN		4.94	2125.1	0.28	122.1	94.3
MAXIMUM		6.43	2764.6	0.61	262.3	97.4
MINIMUM		3.10	1332.9	0.13	55.9	90.0
STD DEV		0.75	323.1	0.12	50.4	2.1
% STD DEV		15.2	15.2	41.3	41.3	2.2

an F factor of 2.63 x 10^{-7} m^3/J (9780 dscf/10^6 Btu). The average inlet SO_2 loading for the test period was 2125 nanograms per Joule (ng/J) or 4.94 pounds per million Btu (lb/10^6 Btu) of heat input to the boiler, whereas the average SO_2 outlet value measured was 122 ng/J (0.28 lb/10^6 Btu). Limited data obtained on February 12 to 16, prior to adding adipic acid, showed a scrubber removal efficiency ranging from 45 to 65 percent.

Analyses of the coal burned during the initial monitor operating period and the test period are shown in Table 5. These data show that the coal sulfur content during the continuous monitoring period ranged from 2.22 to 3.55 percent by weight on a dry basis. Based on these data, the calculated SO_2 emission rate (assuming that 95 percent of the sulfur is converted to SO_2) ranged from 1299 ng/J (3.02 lb/10^6 Btu) to 2210 ng/J (5.14 lb/10^6 Btu).

The average daily feed rates for limestone and adipic acid for the entire test period are shown in Table 6. This table also presents the quantity of coal used per day, which indicates the variation in boiler load. During the monitoring period of March 4 to April 10, 1981, the variation in coal usage from a low of 60.8 Mg/day (55 tons/day) to a high of 138 Mg/day (125 tons/day) reflects the effect of changes in daily temperature on the boiler heat output demand. Of particular interest is the ratio of adipic acid to limestone used to maintain the high SO_2 removal efficiencies during the test; this ratio varied from 6 g/kg (12 lb/ton) to 30 g/kg (60 lb/ton) and averaged 12 g/kg (24 lb/ton).

Table 7 presents data on the concentration of calcium, sulfate, magnesium, and adipic acid in the limestone slurry feed, and the pH of this stream. During the early portion of the test program calcium was in the 2000 to 2500 ppm range. This table also presents the gypsum relative saturation

TABLE 5. COAL COMPOSITION[a]
(%, except as noted)

	Date (1981)											
	2/12	2/13	2/14	2/16	2/17	2/24	3/2-6[b]	3/9-13[b]	3/16-20[b]	3/23-27[b]	3/30-4/3[b]	4/6-10[b]
Sulfur	2.62	2.80	3.00	1.62	2.51	1.64	2.86	3.55	2.85	2.70	2.73	2.22
Carbon	73.06	73.67	69.37	76.23	74.71	74.29	71.48	72.19	74.98	72.61	74.13	75.50
Hydrogen	5.24	5.22	4.72	5.11	5.26	5.30	5.37	5.19	5.37	3.64	5.33	5.61
Oxygen	9.24	8.38	13.84	7.19	7.59	9.06	7.76	7.72	7.83	11.77	9.78	8.99
Nitrogen	1.58	1.56	1.51	1.81	1.64	1.74	1.54	1.56	1.65	1.54	1.49	1.67
Chlorine	0.19	0.21	0.20	0.20	0.18	0.14	0.18	0.12	0.16	0.09	0.09	0.12
Volatile matter	41.65	41.54	41.71	37.47	38.61	37.18	38.99	39.08	40.82	40.01	40.58	40.93
Fixed carbon	50.09	50.09	50.73	54.49	53.10	54.85	50.20	51.25	52.02	52.34	52.97	53.18
Ash	8.26	8.37	7.56	8.04	8.29	7.97	10.81	9.67	7.16	7.65	6.45	5.89
Heat value, kJ/kg (Btu/lb)	31,410 (13,500)	31,040 (13,340)	31,225 (13,420)	31,550 (13,560)	31,410 (13,500)	31,690 (13,620)	30,250 (13,000)	30,510 (13,114)	31,620 (13,590)	31,010 (13,328)	31,240 (13,427)	32,470 (13,955)
Moisture	3.66	3.57	3.81	3.70	2.34	2.02	8.62	7.92	9.35	6.99	6.35	4.26

[a] Dry basis except for moisture.

[b] Composite.

TABLE 6. ADIPIC ACID, LIMESTONE, AND COAL USAGE

Date (1981)		Average adipic acid feed, kg/h (lb/h)[a]	Average limestone feed, kg/h (lb/h)[b]	Mg (tons) of coal used/day
February	20			85.0 (77.1)
	21			90.3 (81.9)
	22			92.7 (84.0)
	23		261 (575)	112.1 (101.6)
	24		281 (619)	126.6 (114.8)
	25		331 (729)	127.8 (115.9)
	26	3.63 (8)	319 (702)	113.4 (102.8)
	27	3.63 (8)	325 (716)	130.4 (118.2)
	28	1.81 (4)	311 (686)	113.5 (102.9)
March	1	1.81 (4)	321 (707)	124.6 (113.0
	2	3.63 (8)	327 (720)	108.6 (98.5)
	3	2.72 (6)	341 (752)	106.1 (96.2)
	4	6.35 (14)	362 (798)	100.8 (91.4)
	5	2.72 (6)	372 (820)	112.6 (102.1)
	6	4.54 (10)[c]	360 (793)	132.0 (119.7)
	7	5.44 (12)[c]	388 (854)	131.4 (119.1)
	8	3.63 (8)[c]	387 (853)	138.1 (125.2)
	9	4.54 (10)[c]	370 (814)	123.1 (111.6)
	10	3.63 (8)	347 (765)	121.1 (109.8)
	11	3.63 (8)	350 (771)	99.9 (90.6)
	12	3.63 (8)	353 (778)	94.6 (85.8)
	13	2.62 (6)	337 (742)	97.5 (88.4)
	14	4.08 (9)	331 (728)	102.1 (92.6)
	15	4.08 (9)	332 (731)	101.1 (91.7)
	16	4.54 (10)	311 (686)	112.3 (101.8)
	17	3.63 (8)	220 (489)	133.2 (120.8)
	18	7.26 (16)[c]	246 (542)	118.5 (107.4)
	19	4.54 (10)	320 (704)	136.4 (123.7)
	20	7.26 (16)[c]	404 (890)	127.1 (115.2)
	21	6.35 (14)[c]	391 (861)	113.2 (102.6)
	22	1.81 (4)[d]	318 (700)	99.2 (89.9)
	23	2.72 (6)	218 (479)	103.2 (93.6)
	24	3.63 (8)	236 (520)	98.8 (89.6)
	25	4.54 (10)	298 (656)	98.5 (89.3)
	26	3.63 (8)	285 (627)	94.2 (85.4)
	27	4.54 (10)	270 (595)	97.9 (88.8)
	28	4.54 (10)	262 (576)	95.1 (86.2)
	29	3.63 (8)	213 (468)	78.4 (71.1)
	30	2.27 (5)[b,e]	184 (405)[e]	69.4 (62.9)
	31	0 (0)[f]	0 (0)[f]	79.9 (72.4)
April	1	6.35 (14)[c]	292 (644)	71.1 (64.5)
	2	5.44 (12)	212 (467)	76.1 (69.0)
	3	3.63 (8)	198 (435)	60.8 (55.1)
	4	3.63 (8)	218 (480)	60.9 (55.2)
	5	1.81 (4)[d]	239 (526)	74.2 (67.3)
	6	4.54 (10)	276 (608)	68.1 (61.7)
	7	4.54 (10)	225 (496)	68.4 (62.0)
	8	2.72 (6)	207 (455)	66.2 (60.0)
	9	2.72 (6)	203 (447)	63.4 (57.5)
	10	2.27 (5)	212 (467)	74.2 (67.3)

[a] 24-hour basis.

[b] Based on hours of feed.

[c] Adipic acid was dumped in the thickener.

[d] Vibrator was turned off. Adipic acid feeder plugged.

[e] Scrubber was bypassed at 1940 because the thickener was plugged. Limestone and adipic acid feeds were turned off at that time.

[f] The scrubber was still off-line. It was restarted before 8:00 a.m. on April 1.

Reproduced from best available copy.

TABLE 7. LIMESTONE SLURRY FEED CONCENTRATIONS, pH, AND GYPSUM RELATIVE SATURATION

Date (1981)	Calcium, mg/liter	Sulfate, mg/liter	Magnesium, mg/liter	Adipic acid concentration, mg/liter	pH	Gypsum relative saturation, %
3/2	-	-	-	1,870	4.74	-
3/3	2,300	2,630	881	1,825	4.87	128.0
3/4	2,460	2,340	854	2,305	4.74	123.5
3/5	2,560	2,350	745	2,920	4.93	127.0
3/6	2,520	2,400	732	2,090	4.71	138.5
3/7	-	-	-	2,290	4.94	-
3/8	-	-	-	2,150	-	-
3/9	2,480	2,220	615	1,770	5.03	126.7
3/10	2,425	2,630	605	2,165	4.98	147.5
3/11	2,400	2,340	585	1,890	4.84	137.7
3/12	2,440	2,570	576	1,855	4.91	151.1
3/13	2,410	2,600	565	1,585	4.91	151.3
3/14	-	-	-	1,870	4.70	-
3/15	-	-	-	2,050	-	-
3/16	2,280	2,410	631	1,890	4.76	127.0
3/17	970	5,320	2,080	1,920	4.25	94.1
3/18	714	9,450	3,300	2,390	4.33	89.4
3/19	786	11,400	3,980	2,430	4.26	102.5
3/20	778	8,940	3,480	3,000	5.2	82.9
3/21	-	-	-	2,680	5.40	-
3/22	1,100	4,340	1,880	2,420	5.38	79.8
3/23	1,080	4,020	1,810	2,090	5.07	80.9
3/24	756	7,620	2,970	2,200	4.68	80.2
3/25	863	6,640	2,670	2,240	5.2	84.7
3/26	1,030	4,600	1,770	2,150	5.3	90.4
3/27	1,180	3,790	1,630	2,130	5.0	90.2
3/28	-	-	-	-	-	-
3/29	-	-	-	-	-	-
3/30	1,170	3,550	1,370	1,920	4.9	98.0
3/31	-	-	-	-	-	-
4/1	1,060	3,090	802	830	5.8	103.6
4/2	1,310	2,610	912	1,950	5.5	92.7
4/3	1,320	2,690	742	2,040	4.8	109.5
4/4	1,260	2,730	939	2,160	4.7	101.3
4/5	-	-	-	2,200	4.6	-
4/6	1,230	3,470	1,220	2,170	5.2	104.5
4/7	1,510	2,880	1,050	2,820	5.1	103.3
4/8	1,340	3,320	1,330	2,850	5.05	97.8
4/9	1,130	3,730	1,890	2,510	4.6	82.1
4/10	1,180	3,740	1,960	2,400	4.7	84.8

values for this stream. Limestone feed rate was reduced on March 16 because the gypsum relative saturation was increasing and scaling might occur. On March 20 the feed rate was again increased. Uniform levels of limestone and adipic acid addition were difficult to maintain because of the use of manual controls, the varying boiler load, and the intermittent discharge of sludge to the holding pond.

CONCLUSIONS

The project resulted in the successful completion of a certified continuous SO_2 monitoring performance test which verified that the addition of adipic acid did enhance the SO_2 removal capability of the Rickenbacker FGD limestone control unit without having any adverse effect on operating parameters. Before the test, this limestone scrubber was achieving about 55 percent SO_2 removal. The adipic acid additive increased the unit's SO_2 removal efficiency to a range of 90 to 97.4 percent and an average of 94.3 percent over a 30-day test period.

ADIPIC ACID-ENHANCED LIME/LIMESTONE TEST RESULTS AT THE EPA ALKALI SCRUBBING TEST FACILITY

Prepared by:

Shih-Chung Wang and Dewey A. Burbank
Bechtel National, Inc.
P. O. Box 3965
San Francisco, CA 94119

EPA Project Officers:

Robert H. Borgwardt
J. David Mobley
John E. Williams

Industrial Environmental Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

EPA Contract No. 68-02-3114

Presented at:

EPA's Industry Briefing on the
Adipic Acid Enhanced Limestone FGD Process

Springfield, MO
July 15, 1981

1. INTRODUCTION AND BACKGROUND

This is the fifth of a series of capsule reports describing the results of the Shawnee Lime and Limestone Wet Scrubbing Test Program conducted by EPA's Industrial Environmental Research Laboratory, Research Triangle Park, North Carolina (IERL-RTP). In this program, flue gas desulfurization (FGD) tests are being conducted at the EPA 10 MW prototype Shawnee Test Facility located at the Tennessee Valley Authority (TVA) coal-fired Shawnee Power Station near Paducah, Kentucky. Bechtel National, Inc. of San Francisco is the major contractor and test director, and TVA is the constructor and facility operator.

This report describes the results of adipic acid-enhanced lime and limestone testing at the Shawnee Test Facility from July 1978 through March 1981. It also summarizes earlier adipic acid additive test results at the IERL-RTP 0.1 MW pilot plant, which led to the testing at Shawnee. Preliminary results from the 100 MW full scale demonstration being conducted at the Southwest Power Plant of Springfield City Utilities, Springfield, Missouri and from the 27 MW equilivent industrial boiler test at Rickenbacker Air Force Base are also reported.

As the emission standards for sulfur dioxide become increasingly stringent and the fossil fueled utilities become hardpressed to meet these standards, there is a strong incentive to improve the FGD system performance while minimizing the operating costs.

A primary objective of the EPA alkali wet scrubbing test program during the last several years has been to enhance SO_2 removal and improve the reliability and economics of lime and limestone wet scrubbing systems by use of adipic acid as a chemical additive.

Adipic acid is a six-carbon dicarboxylic organic acid, $HOOC(CH_2)_4COOH$, that buffers the pH in the scrubber slurry. In theory, any acid which is intermediate in strength between carbonic acid and sulfurous acid and whose calcium salt is reasonably soluble, may be employed. However, adipic acid was selected because it is one of the most cost effective organic acid buffers on a molar basis and is commercially abundant. Its main use is as a raw material in the manufacturing of nylon.

The buffering activity of adipic acid limits the drop in pH that normally occurs at the gas-liquid interface during SO_2 absorption, and the resultant higher concentration of SO_2 at the interface significantly accelerates the liquid-phase mass transfer. The capacity of the bulk liquor for reaction with SO_2 is also increased by the presence of calcium adipate in solution. Thus, the SO_2 absorption becomes less dependent on the dissolution rate of limestone or calcium sulfite in the absorber to provide the necessary alkalinity.

In the case of limestone scrubbing, it logically follows that a given SO_2 removal efficiency can be achieved at a lower limestone stoichiometry thereby improving scrubber reliability.

Adipic acid degrades to lower molecular weight (C_1-C_5) monocarboxcylic acids, paraffinic hydrocarbons and carbon dioxide and water. The feed rate of adipic acid varies depending on the operating conditions, such as pH and oxidation, which influence the degree of degradation, but is usually less than five times the theoretical requirement. Most of the carboxylic acid degradation products, such as valeric acid, still offer proper pH buffer range for effective SO_2 removal enhancement. At Shawnee, all reported concentrations of adipic acid (in ppm) are in reality the concentrations of total carboxylic acid expressed in terms of "adipic acid".

At the Shawnee Test Facility, major emphasis has been placed on the use of adipic acid in conjunction with forced oxidation of calcium sulfite to calcium sulfate since this system results in better sludge dewatering properties and reduced waste solids disposal costs. Furthermore, the more tightly closed liquor loop, achievable as a result of forced oxidation, reduces the adipic acid makeup requirements.

2. ADVANTAGES OF ADIPIC ACID AS SCRUBBER ADDITIVE

A number of attractive features of adipic acid as a scrubber additive are presented below.

HANDLING

Adipic acid is non-toxic, non-hygroscopic, and usually comes in powder form. It is easy to handle and no hazards are encountered in the usual applications other than possible dust explosions which are typical of any organic dust. At Shawnee, it is routinely dry-fed directly to the effluent hold tank, although it has been added to the fresh limestone slurry makeup tank in some instances.

BUFFER REACTION MECHANISM

The mechanism by which adipic acid buffers the pH is simple. It reacts with lime or limestone in the effluent hold tank to form calcium adipate. In the absorber, calcium adipate reacts with absorbed SO_2 (H_2SO_3) to form $CaSO_3$ and simultaneously regenerates adipic acid (the buffer reaction). The regenerated adipic acid is returned to the effluent hold tank for further reaction with lime or limestone. With a sufficiently high concentration of calcium adipate in solution, usually on the order of 10 m-moles/liter to react with the absorbed SO_2, the overall reaction rate is no longer controlled by the dissolution rate of limestone or calcium sulfite.

RETROFIT

Use of adipic acid in an existing lime or limestone system does not require modification of process flow configuration or absorber design; therefore, it is particularly suited for retrofit applications. The fact that it may be added at any point in the slurry circuit provides a greater flexibility in the location and installation of a simple solids storage and feed system, a minimal capital investment.

QUANTITY AND CONCENTRATION

Depending on the operating parameters, the degree of degradation, and the tightness of liquor loop, the quantity of adipic acid required is quite small in relation to the alkali feed. At Shawnee, where a filter is normally used as the final sludge dewatering device, the adipic acid consumption rate is usually less than 10 lb/ton of limestone fed to the system, and sometimes as low as 2 lb/ton of limestone. These values correspond to only 0.6 to 3.0 tons of adipic acid per day for a 500 MW plant.

Adipic acid has two pH buffer points. These are pH 4.5 and 5.5 in the absence of chloride in liquor, and about 4 and 5 with 5000 to 7000 ppm chloride. To fully utilize the buffer capacity of adipic acid, therefore, the slurry pH should be kept above these values. At Shawnee where the chloride concentration is usually a few thousand ppm, a slurry pH above about 5.2 is sufficient to keep adipic acid fully active (or ionized). The optimum concentration range of adipic acid at a pH above 5.2 is only 700 to 1500 ppm for 90% removal of approximately 2500 ppm inlet SO_2. Higher concentration would be required at lower pH to maintain equivalent buffer capacity in the liquid. It should be noted that most of the degradation products of adipic acid, such as valeric amd glutaric acid, are effective buffers.

LIMESTONE UTILIZATION

At a scrubber inlet pH of about 5.2, the corresponding limestone utilization is normally 80 percent or higher for an adipic acid-enhanced system, as compared to 65-70 percent utilization in unenhanced limestone systems at an equivalent SO_2 removal. Thus the quantity of waste solids generated is reduced in an adipic acid-enhanced system. Higher limestone utilization also contributes to more reliable scrubber operation by reducing fouling tendency. This increased reliability is a very attractive feature of adipic acid enhanced systems since reliability problems have historically plagued limestone FGD.

OPERATING pH

With proper pH control and sufficiently high adipic acid concentration (sufficient buffer capacity), the scrubber performance is more stable, and steady outlet SO_2 concentrations can be maintained even with wide fluctuations of inlet SO_2 concentrations.

With the lower operating pH (about 4.6 to 5.4) in an adipic acid-enhanced limestone system, compared to the higher pH (about 5.5-5.8) usually needed for an unenhanced limestone system, the system becomes more amenable to other process concepts and improvements. Potential advantages of low pH operation are:

- Reduced adipic acid consumption. Adipic acid degradation has been found to decrease with decreasing pH.
- Easier forced oxidation in the scrubber slurry loop or bleed stream, and less air (and compressor energy) requirement.
- Essentially complete limestone utilization achievable, with resultant improved scrubber operating reliability.
- Reduced sensitivity to limestone type and grind; fine grinding of limestone is probably not required.

- Lower sulfite scaling potential.
- Better prospects (sensitivity) for automatic pH control.
- Greater flexibility for SO_2 emission control; higher sensitivity of SO_2 removal at lower pH allows raising pH to increase the adipic acid buffer capacity and SO_2 removal when needed.
- Applicability to low sulfur subbituminous and lignite coals containing alkaline ashes which are extractable only at low pH.
- Probable lower cost due to all of the above factors.

ECONOMICS

Since limestone dissolution is not a rate-controlling step in SO_2 absorption for an adipic acid-enhanced limestone system, adipic acid should promote use of less expensive and less energy intensive limestone rather than lime.

Adipic acid-enhanced limestone scrubbing has lower projected capital and operating costs than unenhanced limestone or MgO-enhanced limestone scrubbing. This is primarily due to the reduced limestone consumption at the lower operating pH, the associated reduced grinding cost, and the reduced quantity of waste sludge generated.

FORCED OXIDATION

The mechanism by which adipic acid promotes SO_2 removal is not affected by forced oxidation. Therefore, it can be used with both lime and lime-limestone in systems with or without forced oxidation.

Since forced oxidation converts sulfite to sulfate, it has an adverse effect on SO_2 removal in an unenhanced lime system in which sulfite is a major SO_2 scrubbing species. This is also true in MgO-enhanced lime and limestone systems in which the promotion of SO_2 removal relies on an increased sulfite-bisulfite buffer. When adipic acid is used with lime, calcium adipate becomes a major buffer species; therefore, both good SO_2 removal and sulfite oxidation can be achieved using within-scrubber-loop forced oxidation.

CHLORIDE EFFECT

The effectiveness of adipic acid is not adversely affected by chlorides, as is the effectiveness of MgO in an MgO-enhanced process. Tests at the IERL-RTP pilot plant showed that SO_2 removal efficiency obtained with 17,000 ppm chloride in the scrubbing liquor was not significantly different from that obtained without chloride under similar levels of adipic acid concentration. Thus, use of adipic acid is especially attractive for systems with a very tightly closed liquor loop.

SOLIDS DEWATERING

Adipic acid does not significantly affect the settling and filtration properties of oxidized or unoxidized slurry solids, whereas magnesium does.

TOTAL DISSOLVED SOLIDS

Addition of adipic acid does not significantly increase the total dissolved solids in liquid as does magnesium. High total dissolved solids in liquid entrainment can increase particulate emissions and fouling tendencies of equipment downstream of the scrubber.

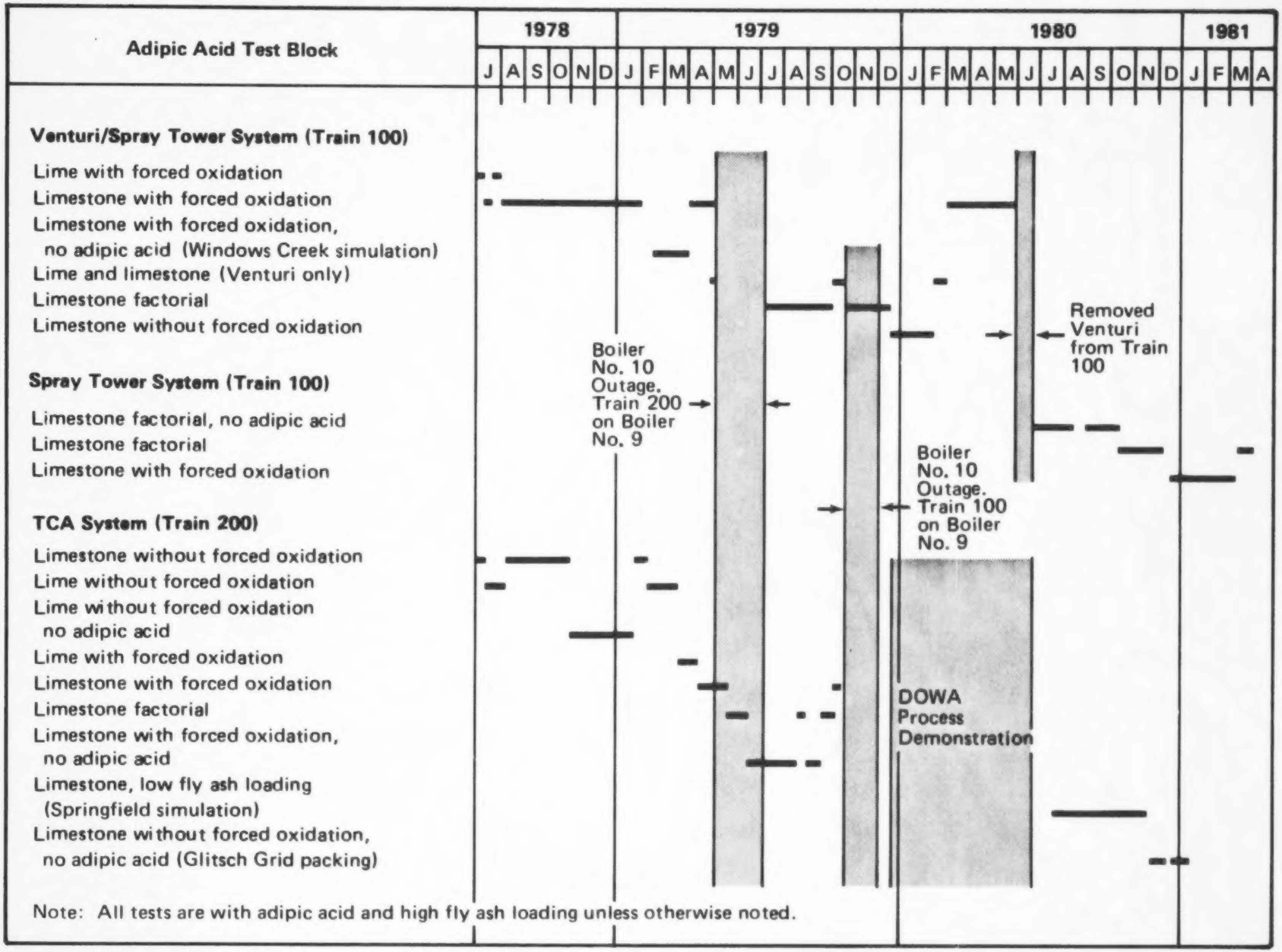
3. TEST PROGRAMS

The theoretical basis for the effect of adipic acid on the performance of lime and limestone scrubbers was first developed in detail by G. Rochelle in 1977 ("The Effect of Additives on Mass Transfer in $CaCO_3$ Slurry Scrubbing of SO_2 from Waste Gases," Industrial and Engineering Chemistry Fundamentals, 16, pp. 67-75, 1977). In October 1977, EPA began investigation of adipic acid with the 0.1 MW IERL-RTP pilot plant to determine its effectiveness as an additive to limestone scrubbers for improving SO_2 removal efficiency. Initial results demonstrated, as predicted by Rochelle, that adipic acid was indeed an attractive and powerful additive.

Based on the findings at the IERL-RTP pilot plant, a program was set up at the 10 MW Shawnee Test Facility to develop commercially usable design data for adipic acid as a chemical additive. Actual testing at Shawnee began in July 1978, and lasted through March 1981. The test schedule for this period is shown in Figure 1. Tests were conducted over a period of 33 months, using both lime and limestone with and without forced oxidation. As can be seen, major emphasis was placed on limestone testing with forced oxidation.

As part of EPA's continuing program of FGD technology transfer, and to further demonstrate the effectiveness of adipic acid and to encourage its use, EPA contracted with Radian Corporation in the spring of 1980 to conduct a full scale demonstration program of adipic acid-enhanced limestone scrubbing. The program was being conducted with two 100 MW Turbulent Contact Absorbers (TCA) located at the Springfield City Utilities' Southwest Station near Springfield, Missouri. Some preliminary test results are included in this report as are data from the industrial-sized (27 MW) scrubber test conducted by PEDCo Environmental, Inc. on the Bahco system at Rickenbacker Air Force Base.

During some factorial tests conducted at the Shawnee Test Facility in 1979, it was noticed that the rate of adipic acid addition required to maintain a desired concentration in the scrubber liquor was substantially reduced when the scrubber inlet pH was controlled at 5.0 or lower. In order to verify the Shawnee findings, the EPA initiated several programs to study the adipic acid degradation phenomenon. Contractors involved included University of Texas at Austin, Radian Corporation, Acurex Corporation, and the Research Triangle Institute. Programs were set up to investigate the effects of pH, oxidation and catalysts, such as manganese and iron, on adipic acid degradation to develop analytical procedures and to identify the degradation products. Although the adipic acid degraation mechanism is complex, the principal variables affecting degradation and its major products have been identified. The results of these studies are beyond the scope of this report.



Note: All tests are with adipic acid and high fly ash loading unless otherwise noted.

Figure 1. Shawnee Adipic Acid Test Schedule

SHAWNEE TEST FACILITY

Tests with adipic acid at Shawnee have been conducted on two parallel scrubber systems: a venturi/spray tower system (Train 100) and a TCA system (Train 200). Each system has its own slurry handling and dewatering facilities and each is designed to remove both SO_2 and particulate from approximately 10 MW equivalent of flue gas (up to 35,000 acfm at 300°F). The flue gas, which normally contains 1400 to 3500 ppm by volume of SO_2, is obtained either upstream (containing high fly ash loading of 2 to 7 grains/dry scf) or downstream (containing low fly ash loading of 0.2 to 0.6 grain/dry scf) from Boiler No. 10 particulate removal equipment.

In June 1980, the venturi scrubber was removed from Train 100, allowing operation with the spray tower only. Previous to the removal of the venturi scrubber, operation with a true spray-tower-only configuration was not possible without some interference from the venturi, even with its adjustable plug wide-open and minimum slurry flow for flue gas cooling.

SHAWNEE TEST BLOCKS

Tests conducted at the Shawnee Test Facility can be classified into blocks according to type of alkali, fly ash loading in the flue gas, adipic acid addition, and forced oxidation scheme. Table 1 lists the combinations of these variables which have been tested at Shawnee, including factorial tests.

Forced oxidation is achieved by air sparging of the slurry in an oxidation tank, either on the bleed stream to the solids dewatering system or on the recirculated slurry within the scrubber slurry loop. For a one-scrubber-loop forced oxidation system, the slurry effluents from all scrubbers in the system (e.g., the venturi scrubber and spray tower at Shawnee constitute a two-scrubber system, and the spray tower alone or TCA a one-scrubber system) are sent to a single effluent hold tank, which is the oxidation tank. For a two-loop forced oxidation system, there are two scrubbers in series (e.g., venturi and spray tower at Shawnee) with effluent from each scrubber going to a separate tank; the effluent hold tank for the upstream scrubber (with respect to gas flow) is the oxidation tank. For either one-loop or two-loop forced oxidation systems, the oxidation tank may be followed by a second tank in series to provide further limestone dissolution and gypsum desupersaturation time prior to recycle to the scrubber.

TABLE 1

TEST BLOCKS CONDUCTED AT SHAWNEE

Test Block	Alkali	Fly Ash Loading	Adipic Acid Addition	Oxidation Scheme	No. of Tanks in Oxid. Loop
Venturi/Spray Tower System:					
1	Lime	High	Yes	2-Loop	2
2	Lime	High	Yes	No	-
3[a]	Limestone	High	Yes	2-Loop	2
4	Limestone	High	Yes	2-Loop	1
5	Limestone	High	Yes	1-Loop	2
6	Limestone	High	Yes	1-Loop	1
7	Limestone	High	Yes	Bleed Stream	-
8	Limestone	High	Yes	No	-
9[b]	Limestone	High	No	2-Loop	2
Spray Tower System:					
10[a]	Limestone	High	Yes	1-Loop	2
11	Limestone	High	Yes	No	-
12	Limestone	High	No	1-Loop	2
13	Limestone	High	No	No	-
TCA System:					
14	Lime	High	Yes	1-Loop	1
15	Lime	High	Yes	No	-
16[a]	Lime	High	No	No	-
17	Limestone	High	Yes	1-Loop	2
18	Limestone	High	Yes	1-Loop	1
19[a]	Limestone	High	Yes	No	-
19[a]	Limestone	High	Yes	No	-
20	Limestone	High	No	1-Loop	1
21[c]	Limestone	High	No	No	-
22[d]	Limestone	Low	Yes	1-Loop	1
23[d]	Limestone	Low	Yes	No	-

(a) Includes long-term (greater than one month) tests
(b) Widows Creek forced oxidation simulation tests
(c) Glitsch Grid packing tests
(d) Springfield adipic acid simulation tests

4. TEST RESULTS

It is beyond the scope of this capsule report to present all of the Shawnee test results from the test blocks listed in Table 1. Therefore, only the typical and important test results are presented below. Results of long-term tests (longer than one month) are included. Results from factorial or partial factorial tests, which normally lasted a minimum of 12 hours including 5 to 7 hours of steady state operation, are also included as figures to illustrate the effects of pH and adipic acid concentration on SO_2 removal.

A summary of initial tests at the IERL-RTP pilot plant and the preliminary results from the full-scale TCA tests at Springfield are also given.

IERL-RTP PILOT PLANT TEST RESULTS

The initial testing of adipic acid as a scrubber additive was carried out by EPA beginning in October 1977 in the 0.1 MW in-house pilot plant located at IERL-RTP. A single-loop limestone scrubber was used for this purpose, operated with forced oxidation in the scrubbing loop. In addition to effects on SO_2 removal and oxidation efficiencies, these tests also sought to determine whether adipic acid caused any change in the properties of the oxidized sludge. So that these properties could be clearly seen, the system was operated without fly ash. Chloride was added as HCl and controlled at the high levels expected for tightly closed loop systems.

The results of the tests showed adipic acid to be very effective in improving SO_2 removal efficiency, even when operating at chloride levels as high as 17,000 ppm. A TCA scrubber, which removed 82 percent of the inlet SO_2 without the additive, yielded 89 percent SO_2 removal with 700 ppm adipic acid, 91 percent removal with 1000 ppm, and 93 percent removal with 2000 ppm adipic acid. The limestone utilization was concurrently increased from 77 percent without the additive, to 91 percent with 1600 ppm adipic acid. The observed effects thus confirmed the theoretical expectations in all respects. In addition, the tests showed no serious interference by adipic acid on the performance of the oxidizer, operating at pH 6.1.

The quality of the oxidized sludge was similar to that obtained when operating without adipic acid, although small differences were detected. For example, the filtered sludge averaged 80 percent solids (for 13 one-week tests) vs. 84 percent solids for 11 tests without the additive, when operating at 97 to 99 percent oxidation in both cases. The settling rate of the slurry (fly ash free at 50°C) averaged 2.3 cm/min during the adipic acid tests and 3.4 cm/min without adipic acid; bulk settled densities averaged 1.0 and 1.2 gm solids/cm^3 slurry, respectively. It was concluded from these results that the large improvements in sludge quality that can be achieved by forced oxidation are not compromised by the use of adipic acid as a scrubber additive.

Tests without forced oxidation also demonstrated the efficacy of adipic acid. Operating a TCA scrubber with 2000 ppm adipic acid and 6 inches H_2O pressure drop, 92 percent SO_2 removal was obtained at a limestone utilization level of 88 percent. By comparison, only 75 percent SO_2 removal would be expected in the pilot plant at these test conditions without the additive. At this adipic acid level the unoxidized sludge filtered to 49 percent solids; at lower adipic acid levels (1500 ppm or less) the filterability of the slurry was the same as that obtained without additives: 55 percent solids.

During the testing with adipic acid, the scrubbing liquor had a noticeable odor even though the additive feed did not. The odor has been identified as valeric acid, $CH_3(CH_2)_3COOH$, which is an intermediate product formed by side reactions that degrade adipic acid at scrubber operating conditons. At Shawnee, this odor was rarely noticed and was not a problem.

LIMESTONE LONG TERM TESTS WITH TWO-SCRUBBER-LOOPS AND FORCED OXIDATION

The venturi/spray tower system was modified for two-scrubber-loop operation with forced oxidation as shown in Figure 2. Two tanks were used in the oxidation loop (venturi loop); air was injected to the first of these tanks through a simple 3-inch diameter pipe below the agitator. Adipic acid was dry-fed to the spray tower effluent hold tank. This was accomplished by manually adding one-pound increments hourly to maintain specified concentration, usually totaling only a few pounds per hour. A small screw feeder would serve the purpose in a full scale plant.

The main advantage of this two-loop system, as far as forced oxidadation is concerned, is that it permits operation of the first loop (venturi loop) at lower pH for good oxidation efficiency while maintaining higher pH in the second loop (spray tower loop) for good SO_2 removal. This configuration also maximizes the limestone utilization. With adipic acid enhancement, however, some of these advantages can also be obtained in a single-loop-scrubber, because an adipic acid-enhanced system can be operated at a lower pH (4.6-5.4). Thus, good oxidation and SO_2 removal both can be achieved without an independent first loop.

Table 2 summarizes the results of two long term (exceeding one month) tests, Runs 907-1A and 907-1B, with adipic acid addition and with a variable gas flow rate. A base case run, Run 901-1A, without additive and with a constant maximum spray tower gas velocity of 9.4 ft/sec, is also included for comparison.

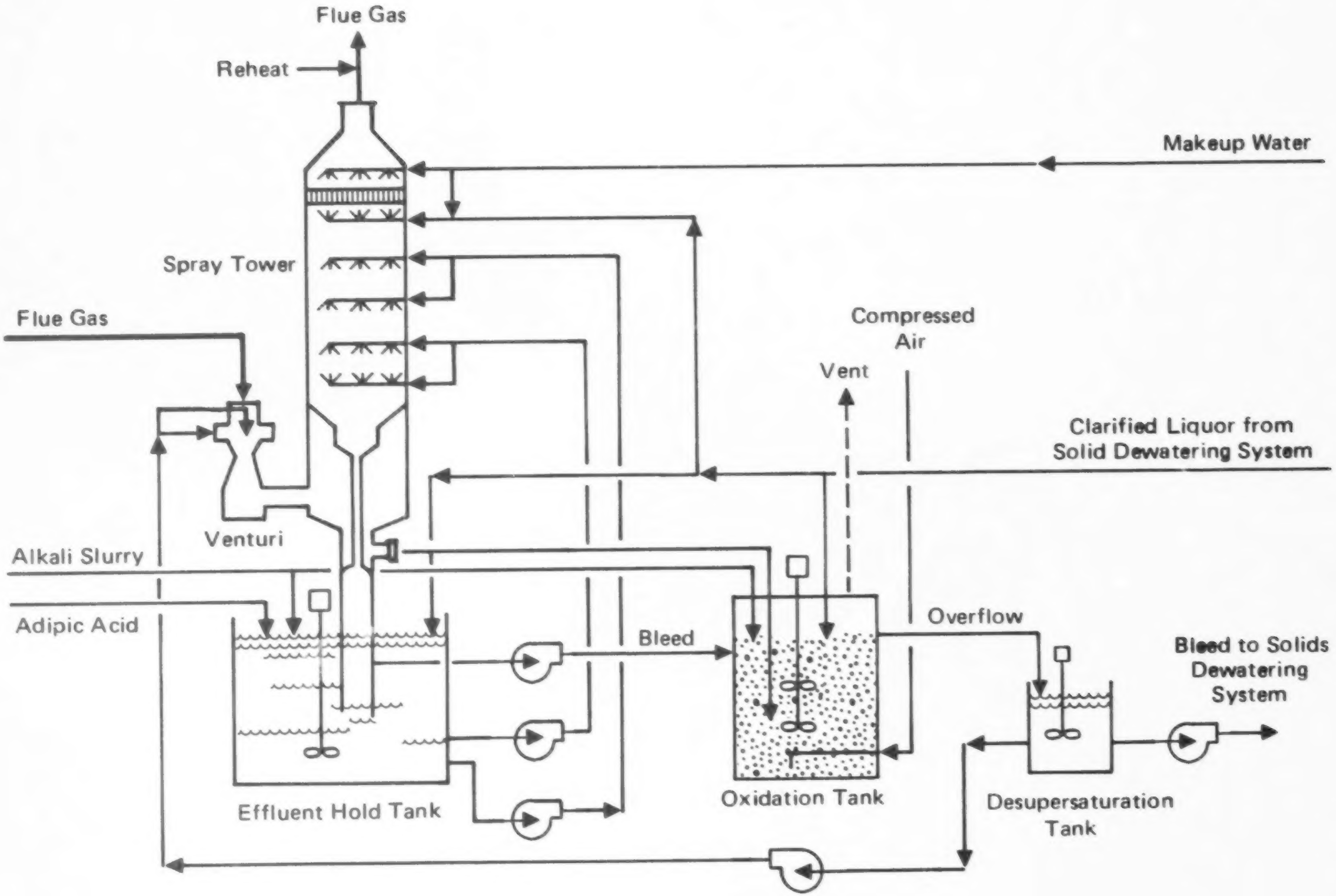

Flue Gas
Reheat
Makeup Water
Spray Tower
Flue Gas
Compressed Air
Vent
Clarified Liquor from Solid Dewatering System
Venturi
Alkali Slurry
Adipic Acid
Bleed
Overflow
Bleed to Solids Dewatering System
Effluent Hold Tank
Oxidation Tank
Desupersaturation Tank

Figure 2. Flow Diagram for Adipic Acid-Enhanced Scrubbing in the Venturi/Spray Tower System with Two Scrubber Loops and Forced Oxidation

Table 2

ADIPIC ACID-ENHANCED LIMESTONE TESTS ON THE TWO-LOOP VENTURI/SPRAY TOWER SYSTEM WITH FORCED OXIDATION

Run No.	901-1A	907-1A	907-1B
Onstream hours	187	719	1666
Fly Ash Loading	High	High	High
Adipic Acid Conc. in Venturi, ppm	0	2360	2180
Adipic Acid Conc. in Spray Tower, ppm (controlled)	0	1560	1510
Spray Tower Gas Velocity, ft/sec	9.4	4.8-9.4	5.4-9.4
Venturi Liquid-to-Gas Ratio, gal/Mcf	21	21-42	21-37
Spray Tower Liquid-to-Gas Ratio, gal/Mcf	57	57-111	57-100
Venturi Slurry Solids Conc., wt% (controlled)	15	15	15
Spray Tower Slurry Solids Conc., wt%	5.9	6.1	5.9
Venturi Inlet pH (controlled)	4.50	4.65	4.65
Spray Tower Inlet pH	5.45	5.45	5.35
Ventrui Pressure Drop, in. H_2O	9.0	3.0-9.6	3.5-9.2
Oxidation Tank Level, ft	18	18	18
Oxidation Tank Residence Time, min	11.3	11.3	11.3
Desupersaturation Tank Residence Time, min	4.7	4.7	4.7
Spray Tower Effluent Tank Residence Time, min	14.7	14.7	14.7
Spray Tower Limestone Stoich. Ratio (controlled)	1.36	1.77	1.70
Average Percent SO_2 Removal	57	97.5	97
Average Inlet SO_2 Concentration, ppm	2800	2350	2500
Percent Oxidation of Sulfite to Sulfate	98	98.5	98
Air Stoichiometry, atoms oxygen/mole SO_2 absorbed	2.30	2.0-3.85	1.9-3.3
Overall Percent Limestone Utilization	97	88	92
Venturi Inlet Liquor Gypsum Saturation, %	95	110	105
Spray Tower Inlet Liquor Gypsum Saturation, %	95	105	110
Filter Cake Solids Content, wt%	85	87	85

Run 907-1A was a month-long adipic acid enhanced limestone run with forced oxidation designed to demonstrate operational reliability with respect to scaling and plugging and to demonstrate the removal enhancement capability of the adipic acid additive. This run was controlled at a nominal limestone stoichiometry of 1.7 (compared to 1.4 for the base case run, Run 901-1A) and 1500 ppm adipic acid in the spray tower. Venturi inlet pH was controlled at a minimum of 4.5 by the occasional addition of limestone to the venturi loop.

Flue gas flow rate was varied from 18,000 acfm to a maximum of 35,000 acfm (spray tower gas velocity between 4.8 and 9.4 ft/sec) to follow the daily boiler load cycle which normally fluctuated between 100 and 150 MW. The adjustable venturi plug was fixed in a position such that the pressure drop across the venturi was 9 inches H_2O at 35,000 acfm maximum gas rate. Actual pressure drop ranged from 3.0 to 9.6 inches H_2O.

The slurry recirculation rates to the venturi and spray tower were fixed at 600 gpm (L/G = 21 to 42 gal/Mcf) and 1600 gpm (L/G = 57 to 111 gal/Mcf), respectively.

The oxidation tank level was 18 ft and the air flow rate was held constant at 260 scfm.

The run began on October 8, 1978 and terminated November 13, 1978. It ran for 719 onstream hours (30 days) with no unscheduled outages. The scrubber was down once for a scheduled 3-hour inspection and again when the boiler came down for 135 hours to install a new station power transformer.

Average SO_2 removal for Run 907-1A was 97.5 percent at 2350 ppm average inlet SO_2 concentration. The SO_2 removal stayed within a narrow range of 96 to 99 percent throughout almost the entire run. This was a significant improvement over the 57 percent SO_2 removal for the base case run, Run 901-1A, at 9.4 ft/sec spray tower gas velocity under similar conditions. On October 19 and on October 27, SO_2 removal dropped briefly to less than 90 percent when the pump which supplies the slurry to the top two spray headers was brought off stream for repacking and the spray tower slurry flow rate was cut in half to 800 gpm. At the reduced slurry recirculation rate, SO_2 removal was 82 to 87 percent.

Venturi and spray tower inlet pH averaged 4.65 and 5.45, respectively. Overall limestone utilization was 88 percent and the spray tower limestone utilization was 56 percent, demonstrating the advantage of good limestone utilization in a two-scrubber-loop operation.

Average adipic acid concentrations were 2360 ppm in the venturi loop and 1560 ppm in the spray tower loop.

Sulfite oxidation in the system bleed slurry averaged 98.5 percent with the air stoichiometric ratio varied between 2.0 and 3.85 atoms oxygen/mole SO_2 absorbed. The filter cake solids content was 87 percent.

The mist eliminator was clean during the entire run. The system was free of plugging and scaling and there was no increase in solids or scale deposits on the scrubber internals during Run 907-1A.

Following Run 907-1A, a second adipic acid-enhanced limestone long term run with forced oxidation was made during which flue gas monitoring procedures were evaluated by EPA. This run, Run 907-1B, was made under the same conditions as Run 907-1A except that a "typical" daily boiler load cycle was established for the gas flowrate rather than depending on a ratio to the Unit No. 10 Boiler load.

Run 907-1B began on November 13, 1978 and terminated January 29, 1979. It ran for 1666 onstream hours (69 days) with only 27 hours of scrubber related outages. The scrubber was also out of service 146 hours when Unit 10 came down for replacement of a broken turbine thrust bearing.

Excluding boiler outages and scheduled inspections, the combined Runs 907-1A and 907-1B operated for a period of over 3 months with an onstream factor of 98.9 percent. No deposits whatsoever were observed in the mist eliminator for the entire 3-month test period. On only one occasion did solids accumulation cause an outage; the cross-over line carrying slurry effluent from the venturi to the oxidation tank plugged with soft solids and had to be cleaned out. Because of problems associated with converting the Shawnee venturi/spray tower system to two-scrubber-loop operation, this cross-over line follows a tortuous path (see Figure 2). A properly designed system would not have this problem.

Results of Run 907-1B were as good in every respect as those of Run 907-1A. Average SO_2 removal remained within a narrow band of 95 to 99 percent. SO_2 removal dropped briefly (typically 30 minutes) below 90 percent five times when one of the two spray tower recirculation pumps was taken out of service for maintenance, effectively cutting the slurry recirculation rate in half.

Overall limestone utilization during this run was 92 percent. Sulfite oxidation averaged 98 percent and the waste sludge filter cake quality was excellent, having a solids content of 85 percent.

SO_2 emissions for Run 907-1A and 907-1B were calculated based on an assumed coal heating value of 10,500 Btu/lb, on 100 percent sulfur overhead (none in bottom ash), and on an assumed excess air of 30 percent. This excess air rate results in about 700 ppm inlet SO_2 per 1.0 weight percent sulfur in coal for the above conditions. The average SO_2 emission for the entire 3-month operating period was only 0.20 lb/MM Btu. The highest 24-hour average SO_2 emission during Run 907-1A was 0.37 lb/MM Btu and during Run 907-1B was 0.41 lb/MM Btu.

A material balance calculation for the adipic acid consumption was made for Run 907-1B. Actual adipic acid feed rate was 8.3 lb/ton of limestone fed to the system, of which 1.8 lb/ton were discharged with the filter cake (theoretical requirement) and 6.5 lb/ton were unaccounted for, giving an actual-to-theoretical consumption ratio of 4.6.

LIMESTONE LONG TERM TEST WITH ONE-SCRUBBER-LOOP AND WITHOUT FORCED OXIDATION

Perhaps the most straightforward illustration of the effectiveness of adipic acid is demonstrated by a long-term limestone test conducted on the Shawnee TCA system, in which the additive was introduced without any system modifications.

Table 3 lists the results of the long term test, Run 932-2A, with adipic acid enhancement. A base case run, Run 926-2A, without the additive, is also included in the table for comparison.

Figure 3 depicts the simple single-loop, one-tank configuration of the TCA system used for these runs. The TCA contained three beds of 1-7/8 inch diameter, 11.5 gram nitrile foam spheres retained between bar grids. Each bed contained 5 inches static height of spheres. Adipic acid was manually fed by the operator to the effluent hold tank.

Run 932-2A was made to demonstrate both operational reliability with respect to scaling and plugging of the TCA and the SO_2 removal enhancement capability of the adipic acid additive. The run began on September 26, 1978 and terminated on November 2, 1978 for a total of 833 onstream hours (35 days). During the run, the scrubber was out of service for 48 hours due to a boiler outage caused by a tube leak, 5 hours for a scheduled inspection and 8 hours for unscheduled outages to clean and repair the scrubber induced-draft fan damper. Excluding boiler outages and scheduled inspections, Run 932-2A operated with an onstream factor of 99.0 percent. As was typical of all long term runs, the scrubber was more reliable than the boiler.

The run was controlled at a nominal limestone stoichiometric ratio of 1.2 and 1500 ppm adipic acid concentration in the slurry liquor. Slurry solids concentration was controlled at 15 percent. The flue gas flow rate was varied between 20,000 and 30,000 acfm (8.4 to 12.5 ft/sec superficial gas velocity) as the boiler load fluctuated between 100 and 150 MW. The slurry recirculation rate was fixed at 1200 gpm (L/G = 50 to 75 gal/Mcf). The effluent hold tank residence time was only 4.1 minutes.

Table 3

ADIPIC ACID-ENHANCED LIMESTONE TEST ON THE SINGLE-LOOP TCA SYSTEM WITHOUT FORCED OXIDATION

Run No.	926-2A	932-2A
Onstream Hours	192	833
Fly Ash Loading	High	High
Adipic Acid Concentration, ppm (controlled)	0	1620
Scrubber Gas Velocity, ft/sec	12.5	8.4-12.5
Liquid-to-Gas Ratio, gal/Mcf	50	50-75
Slurry Solids Concentration, wt% (controlled)	15	15
Limestone Stoichiometric Ratio (controlled)	1.2	1.2
Total Static Bed Height, inches of 11.5 gram nitrile spheres	15	15
Effluent Hold Tank Residence Time, min.	4.1	4.1
Average Percent SO_2 Removal	71	96
Average Inlet SO_2 Concentration, ppm	2750	2450
SO_2 Make-Per-Pass, M-moles/liter	10.1	4-18
Percent Oxidation of Sulfite to Sulfate	13	21
Scrubber Inlet pH	5.65	5.30
Percent Limetone Utilization	80	82
Scrubber Inlet Liquor Gypsum Saturation, %	90	110
Centrifuge Cake Solids Content, wt %	37*	61

* Clarifier underflow solids content.

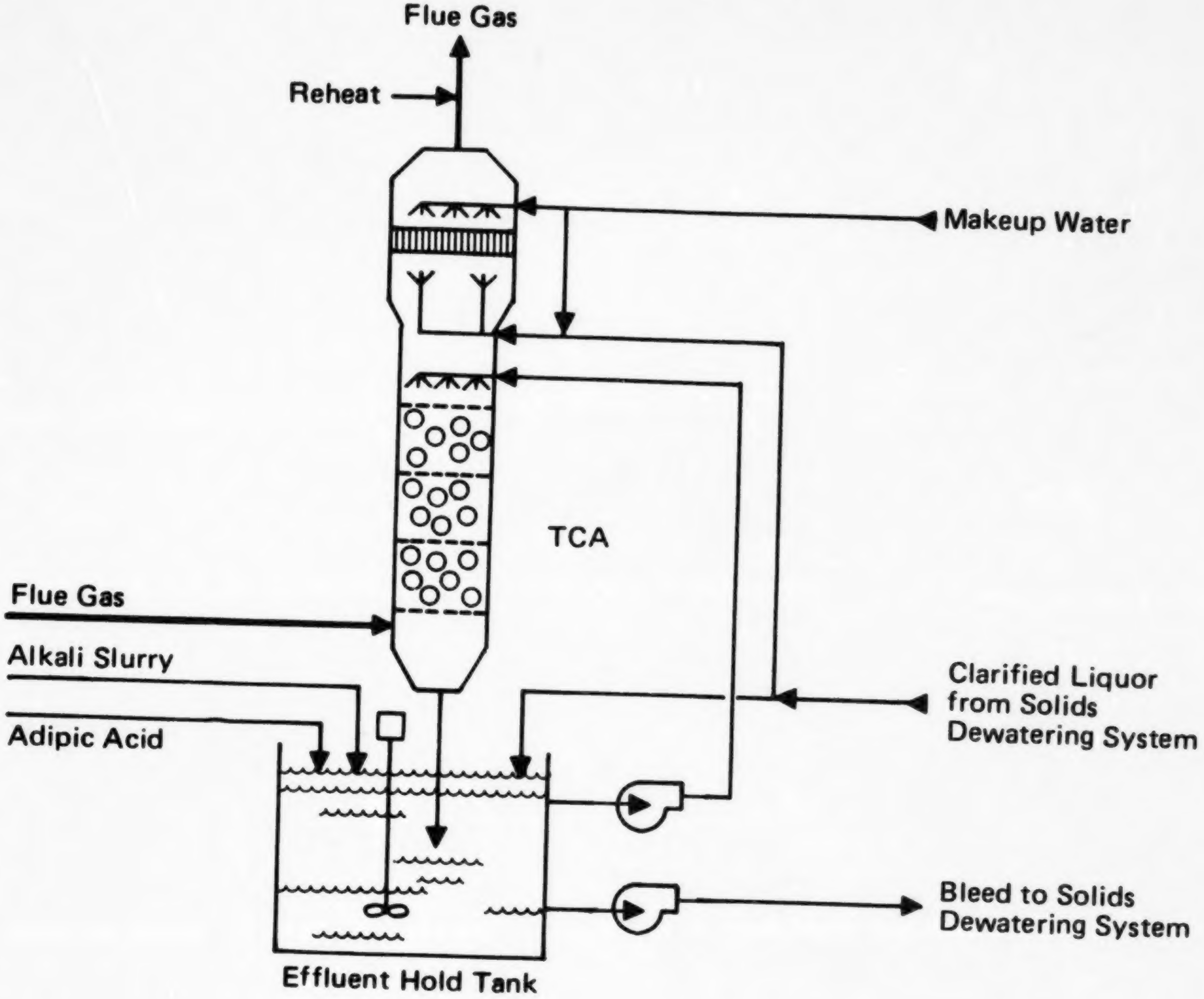

Flue Gas
Reheat
Makeup Water
TCA
Flue Gas
Alkali Slurry
Adipic Acid
Clarified Liquor
from Solids
Dewatering System
Bleed to Solids
Dewatering System
Effluent Hold Tank

Figure 3. Flow Diagram for Adipic Acid-Enhanced Scrubbing in the TCA System without Forced Oxidation

SO_2 removal during Run 932-2A averaged 96 percent at an average inlet SO_2 concentration of 2450 ppm. Excluding the first few days of unsteady state operation, SO_2 removal stayed within the narrow range of 94 to 98 percent as the inlet SO_2 concentration varied widely between 1400 and 3500 ppm. By contrast, SO_2 removal during the base case run without adipic acid, Run 926-2A, averaged only 71 percent at 2750 ppm average inlet SO_2 concentration and at constant 12.5 ft/sec gas velocity and 50 gal/Mcf liquid-to-gas ratio.

SO_2 emissions were calculated for Run 932-2A on the same basis as for the venturi/spray tower runs, Runs 907-1A and 907-1B. Excluding the first few days of unsteady state operation, the SO_2 emissions for the 27-day period from October 6 through the end of the run on November 2, 1978, averaged only 0.26 lb/MM Btu. The highest 24-hour average SO_2 emission during this period was only 0.44 lb/MM Btu.

The mist eliminator was completely clean at the end of Run 932-2A and the entire scrubber system was free of scaling and plugging. Limestone utilization during the run averaged 82 percent. Solids discharged from the centrifuge averaged about 61 percent which is typical of unoxidized limestone sludge.

An adipic acid material balance calculation was made for a 21 day period during Run 932-2A. The actual adipic acid feed rate was 9.2 lb/ton limestone feed, of which 4.2 lb/ton were discharged with the centrifuge cake (theoretical requirement) and 5.0 lb/ton were unaccounted loss, giving an actual-to-theoretical consumption ratio of 2.2. This ratio was less than the value of 4.6 for venturi/spray tower Run 907-1B when oxidation was forced, indicating that forced oxidation promotes adipic acid degradation. However, the actual feed rate of 9.2 lb/ton limestone for Run 932-2A was higher than the 8.3 lb/ton limestone for Run 907-1B, because of the higher moisture content in the discharge cake for Run 932-2A without forced oxidation. Thus, the net effect of forced oxidation was to reduce the adipic acid makeup requirements by approximately 10 percent.

In summary, the objectives of this long term test were met. High removal was consistently achieved at a good limestone utilization and no fouling, scaling, or plugging occurred.

LIME TEST WITH ONE-SCRUBBER-LOOP AND WITHOUT FORCED OXIDATION

Tests with adipic acid in lime scrubbing also were impressive in enhancing SO_2 removal, both on the venturi/spray tower and TCA systems. Table 4 shows some typical results of adipic acid-enhanced lime tests from the Shawnee TCA without forced oxidation. The flow diagram for these tests is shown in Figure 3.

Table 4

ADIPIC ACID-ENHANCED LIME TESTS ON THE SINGLE-LOOP TCA SYSTEM WITHOUT FORCED OXIDATION

Run No.	978-2A	979-2A	980-2A
Onstream Hours	116	177	247
Fly Ash Loading	High	High	High
Adipic Acid Concentration, ppm (controlled)	0	615	1305
Scrubber Gas Velocity, ft/sec	12.5	12.5	12.5
Liquid-to-Gas Ratio, gal/Mcf	50	50	50
Slurry Solids Concentration, wt% (controlled)	8	8	8
Scrubber Inlet pH (controlled)	7.0	7.2	6.95
Total Static Bed Height, inches of 11.5 gram nitrile spheres	15	15	15
Effluent Hold Tank Residence Time, min	4.1	4.1	4.1
Average Percent SO_2 Removal	83	93	97.5
Average Inlet SO_2 Concentration, ppm	2350	2900	2750
SO_2 Make-Per-Pass, m-moles/liter	10.3	14.3	14.3
Percent Oxidation of Sulfite to Sulfate	21	14	10
Percent Lime Utilization	92	92	88
Scrubber Inlet Liquor Gypsum Saturation, %	125	90	75

All three runs listed in Table 4 were operated under the same conditions except for the adipic acid concentration. Run 978-2A was a base case test without adipic acid. For Runs 979-2A and 980-2A, adipic acid concentration was controlled at a nominal 600 ppm and 1200 ppm, respectively (615 ppm and 1305 ppm actual). The scrubber inlet pH was controlled at 7.0 for all runs.

Average SO_2 removal improved from 83 percent at 2350 ppm average inlet SO_2 concentration for the base case run, to 93 percent SO_2 removal at higher inlet SO_2 concentration of 2900 ppm with 615 ppm adipic acid, and to 97.5 percent removal at 2750 ppm inlet SO_2 with 1305 ppm of adipic acid. Thus, with 600 to 1300 ppm of adipic acid, SO_2 removal improved by 10 to 15 percent over the base case removal of 83 percent at 50 gal/Mcf liquid-to-gas ratio and 7.0 scrubber inlet pH.

LIME TEST WITH ONE-SCRUBBER-LOOP AND FORCED OXIDATION

Within-scrubber-loop forced oxidation in a single-loop scrubbing system would not be expected to give good SO_2 removal for a lime scrubber because of the oxidation of the major scrubbing species, sulfite ion, into non-reactive sulfate ion. With adipic acid addition, however, satisfactory SO_2 removal should be possible because calcium adipate becomes the major scrubbing species. In addition, the lower pH at which a lime/adipic acid system operates should facilitate sulfite oxidation.

Table 5 lists the test results of such a lime run, Run 951-2E, using within-scrubber-loop forced oxidation with 1330 ppm adipic acid. The system configuration used for this run was the same as that shown in Figure 3, except that the oxidizing air was injected into the effluent hold tank (oxidation tank). A single 3-inch diameter pipe was used for this purpose, with the air discharging downwards at the center of the oxidation tank 5 inches from the tank bottom.

Run 951-2E was made with a scrubber inlet pH of 5.0 (oxidation tank pH). Higher pH increases the calcium sulfite scaling tendency and also decreases oxidation efficiency. Lower pH reduces the calcium adipate buffer capacity and SO_2 removal efficiency.

At 5.0 scrubber inlet pH and 50 gal/Mcf liquid-to-gas ratio, sulfite oxidation averaged 98 percent and the SO_2 removal was satisfactory at 82 percent.

It should be noted that under the operating conditions chosen for Run 951-2E, the major SO_2 scrubbing species is calcium adipate because there is little sulfite available, both in liquor or solids, which would normally be the major scrubbing species in an unenhanced lime system without forced oxidation. Higher SO_2 removal than the

Table 5

ADIPIC ACID-ENHANCED LIME TEST ON THE SINGLE-LOOP TCA SYSTEM WITH FORCED OXIDATION

Run No.	951-2E
Onstream Hours	103
Fly Ash Loading	High
Adipic Acid Concentration, ppm (controlled)	1330
Scrubber Gas Velocity, ft/sec	12.5
Liquid-to-Gas Ratio, gal/Mcf	50
Slurry Solids Concentration, wt% (controlled)	8
Scrubber Inlet pH (controlled)	5.0
Total Static Bed Height, inches of 11.5 gram nitrile spheres	15
Oxidation Tank Level, ft	17
Oxidation Tank Residence Time, min	4.1
Average Percent SO_2 Removal	82
Average Inlet SO_2 Concentration, ppm	2400
SO_2 Make-Per-Pass, m-moles/liter	10.4
Percent Oxidation of Sulfite to Sulfate	98
Air Stoichiometry, atoms oxygen/mole SO_2 absorbed	1.95
Percent Lime Utilization	97
Scrubber Inlet Liquor Gypsum Saturation, %	105
Scrubber Inlet Liquor $SO_3^=/HSO_3^-$ Concentration, ppm	100
Centrifuge Cake Solids Content, wt %	72

82 percent in Run 951-2E should be achievable by simply raising the adipic acid concentration beyond the 1330 ppm tested.

An SO_2 removal of only 65 percent would be predicted under the same operating conditions as Run 951-2E but without forced oxidation and without adipic acid addition. With forced oxidation and without adipic acid enhancement, the expected SO_2 removal should be significantly lower than 65 percent.

LIMESTONE LONG TERM TEST WITH ONE-SCRUBBER-LOOP AND FORCED OXIDATION

A one-scrubber-loop system has inherent advantage over a two-scrubber-loop system in its simple design and lower capital and operating costs. If a simple one-loop limestone (or lime) system is operated with adipic acid which offers the advantage of lower operating pH, then both good SO_2 removal and sulfite oxidation can be achieved with minimum cost.

This was illustrated in a long-term adipic acid-enhanced limestone run, Run 917-1A, conducted on the Shawnee spray tower system from December 26, 1980, to March 13, 1981. Figure 4 shows the flow diagram for this long term run with forced oxidation using two series tanks in the slurry loop. Oxidation is forced in the first tank while fresh limestone is added to the second. Use of two tanks in series in a within-scrubber-loop forced oxidation system has several advantages over a single tank:

- Lower pH in the first tank (oxidation tank), which receives the scrubber effluent slurry and gives better oxidation efficiency.
- Potential of limestone blinding by calcium sulfite is reduced because liquor sulfite is oxidized in the first tank before fresh limestone is added to the second tank.
- Limestone utilization is improved with two tanks in series.
- The second tank offers extra time for gypsum desupersaturation and precipitation.
- The second tank provides air-free suction for slurry recirculation pumps.

In any within-scrubber-loop forced oxidation system, irrespective of whether it is additive promoted or not, the possibility exists for calcium sulfite blinding of limestone because the recirculated slurry lacks the solid $CaSO_3$ crystal seeds. Under this environment, and if the oxidation intensity is not sufficiently high, liquor sul-

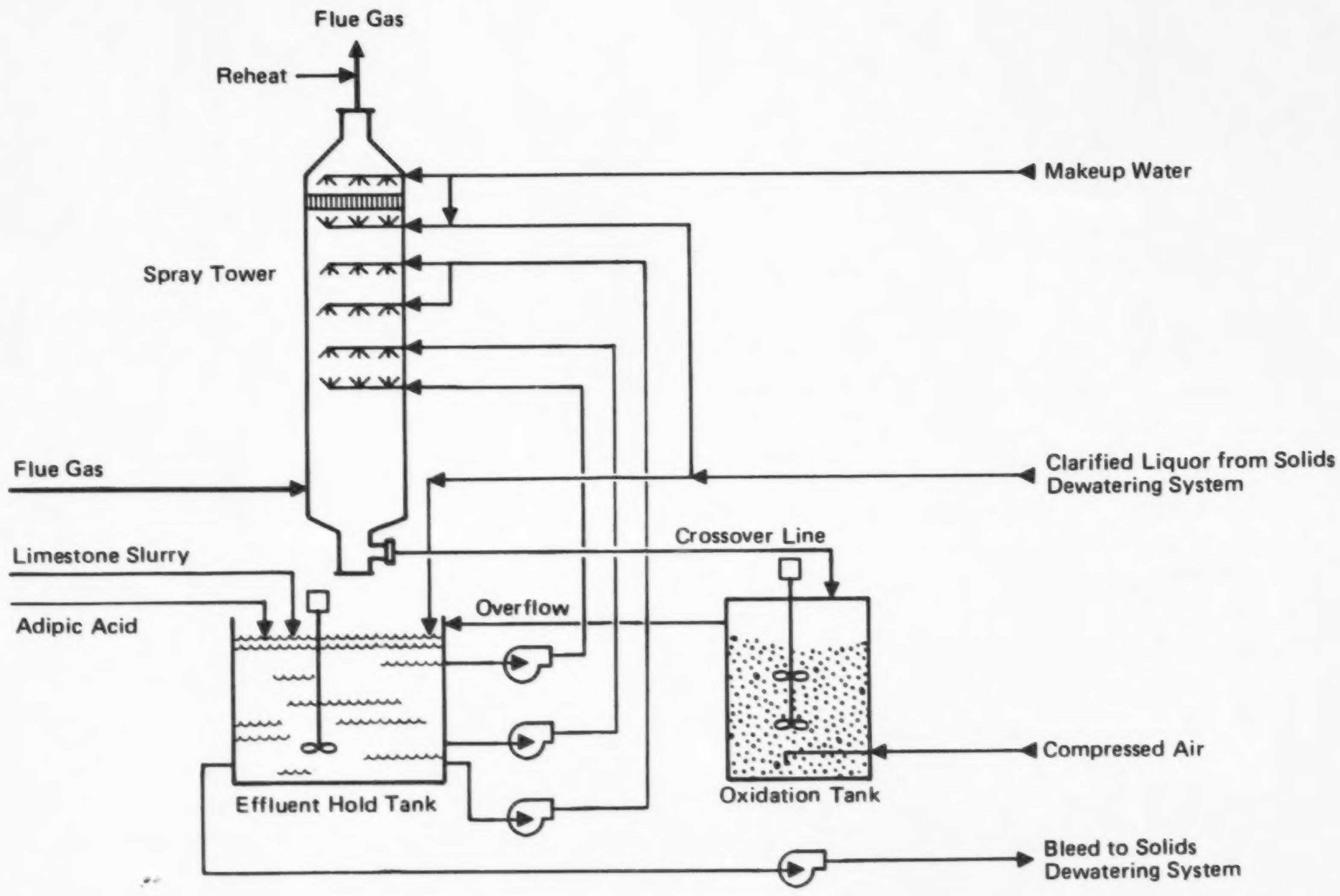

Flue Gas
Reheat
Spray Tower
Makeup Water
Flue Gas
Clarified Liquor from Solids Dewatering System
Crossover Line
Limestone Slurry
Adipic Acid
Overflow
Effluent Hold Tank
Oxidation Tank
Compressed Air
Bleed to Solids Dewatering System

Figure 4. Flow Diagram for Adipic Acid-Enhanced Limestone Scrubbing in the Spray Tower System with Forced Oxidation and Two Tanks

fite could build up to a level at which $CaSO_3$ begins to precipitate on alkaline limestone particles, causing limestone blinding, reduced dissolution and a pH drop. The problem is usually avoided by increasing the air stoichiometry to prevent the buildup of sulfite in the liquor. The potential of limestone blinding is further reduced by the use of two tanks in series as described above to permit sulfite oxidation before limeston addition.

Table 6 summarizes the important test results of Run 917-1A. As in the previous runs with forced oxidation air was injected into the oxidation tank through a single 3-inch diameter pipe. The system was onstream for 1688 hours. During the run, the scrubber was out of service for 78 hours due to equipment problems and 84 hours due to boiler outages. Excluding boiler outages, Run 917-1A operated with an on stream factor of 95.6 percent.

The run was controlled at a scrubber inlet pH of 5.0 to 5.1 and an adipic acid concentration of 1300 to 1700 ppm to obtain 90 percent or higher SO_2 removal. The flue gas flow rate was varied between 20,000 and 35,000 acfm (5.4 to 9.4 ft/sec superficial gas velocity) according to a "typical daily boiler load cycle". The slurry flow rate was fixed at 2400 gpm (L/G = 85 to 150 gal/Mcf). Slurry solids concentration was controlled at 15 percent.

SO_2 removal during the run averaged 93.4 percent at 2660 ppm average inlet SO_2 concentration. At the low L/G of 85 gal/Mcf, SO_2 removal varied from 87 to 92 percent with 1300 ppm adipic acid and from 90 to 93 percent with 1700 ppm adipic acid. At the high L/G of 150 gal/Mcf, the removal was 97 to 99 percent. Daily average SO_2 removal was 92 to 95 percent.

Limestone utilization averaged 92.6 percent. Sulfite oxidation was excellent at 99.8 percent and the filter cake solids content was high, averaging 86 percent. Gypsum saturation in the scrubber inlet liquor was only 93 percent.

The mist eliminator was completely clean at the end of the run and there was no evidence of plugging or scaling within the spray tower.

The actual adipic acid consumption rate during Run 917-1A was only 5.4 lb/ton of limestone feed, four times the theoretical requirement.

LIMESTONE TEST WITH BLEED STREAM OXIDATION

A major advantage of the bleed stream oxidation is its simple flow configuration. In operation without forced oxidation, the scrubber bleed stream would be sent directly to the solids dewatering system. To oxidize this bleed stream, it is necessary only to install an oxidation tank and the associated agitator and compressed air system anywhere between the effluent hold tank and the solids dewater-

Table 6

ADIPIC ACID-ENHANCED LIMESTONE TEST ON THE SINGLE-LOOP SPRAY TOWER SYSTEM WITH FORCED OXIDATION AND TWO TANKS

Run No.	917-1A
Onstream Hours	1688
Fly Ash Loading	High
Adipic Acid Concentration, ppm (controlled)	1300-1700
Scrubber Gas Velocity, ft/sec	5.4-9.4
Liquid-to-Gas Ratio, gal/Mcf	85-150
Slurry Solids Concentration, wt% (controlled)	15
Scrubber Inlet pH (controlled)	5.0-5.1
Oxidation Tank Level, ft	18
Oxidation Tank Residence Time, min	2.8
Effluent Hold Tank Residence Time, min	8.3
Average Percent SO_2 Removal	93.4
Average Inlet SO_2 Concentration, ppm	2660
SO_2 Make-Per-Pass, m-moles/liter	4.0-8.9
Percent Oxidation of Sulfite to Sulfate	99.8
Air Stoichiometry, atoms oxygen/mole SO_2 absorbed	1.4-2.4
Oxidation Tank pH	4.9
Percent Limestone Utilization	92.6
Scrubber Inlet Liquor Gypsum Saturation, %	93
Filter Cake Solids Content, wt %	86

ing area. Thus, the bleed stream oxidation scheme is particularly well suited for retrofit when modifications of the existing scrubber system for within-scrubber-loop forced oxidation are not possible due to physical constraints.

Bleed stream oxidation of unenhanced lime or limestone slurry is usually not feasible, because the pH rise caused by the residual alkali in the oxidation tank makes it difficult to redissolve the solid calcium sulfite. With adipic acid enhanced limestone scrubbing, however, this constraint is removed because of the low operating pH and low residual alkali in the bleed slurry. Thus, the oxidation tank can be maintained at a low pH for good sulfite oxidation while achieving high SO_2 removal efficiency with a sufficiently high concentration of adipic acid in the scrubber liquor.

Table 7 gives the results of a typical bleed stream oxidation test, Run 915-1C, which was conducted with adipic acid enhanced limestone on the venturi/spray tower system. The effluent slurries from the venturi and the spray tower were discharged into a common effluent hold tank. The scrubber bleed stream was pumped from the effluent hold tank to an oxidation tank into which air was injected through a 3-inch diameter pipe. The final system bleed was withdrawn from the oxidation tank and sent to the solids dewatering system.

Good sulfite oxidation of 98 percent was achieved in the oxidation tank at 4.8 pH and 1.8 air stoichiometry. SO_2 removal was high at 96 percent with 4.8 scrubber inlet pH, 4140 ppm adipic acid, and 2030 ppm inlet SO_2 concentration.

Degradation of adipic acid was low, as expected with the low pH operation. The actual-to-theoretical adipic acid consumption ratio was only 1.26 for a rate of 8.7 lb/ton of limestone feed. The centrifuge cake solids content was 79 percent.

FACTORIAL TEST RESULTS

Full or partial factorial tests have been conducted at Shawnee primarily to investigate the effects of adipic acid concentration and pH on SO_2 removal. These tests usually lasted 12 hours or longer, including at least 5 to 7 hours of steady-state operation. Scrubber configurations used were: venturi alone, spray tower alone, combined venturi and spray tower, and TCA. Limestone was used in all scrubber configurations. Lime was used only with the venturi alone. Only the typical results from the TCA and spray tower tests are presented below to show the degree of effect of pH and adipic acid concentration on SO_2 removal.

Figures 5 through 7 show the results of partial factorial limestone runs conducted on the TCA system using two tanks in series. Operating conditions common to all runs were:

Table 7

ADIPIC ACID-ENHANCED LIMESTONE TEST ON THE VENTURI/SPRAY TOWER SYSTEM WITH BLEED STREAM OXIDATION

Run No.	915-1C
Onstream Hours	127
Fly Ash Loading	High
Adipic Acid Concentration, ppm (controlled)	4140
Spray Tower Gas Velocity, ft/sec	9.4
Venturi Liquid-to-Gas Ratio, gal/Mcf	21
Spray Tower Liquid-to-Gas Ratio, gal/Mcf	57
Slurry Solids Concentration, wt% (controlled)	15
Scrubber Inlet pH (controlled)	4.8
Venturi Pressure Drop, in. H_2O	9
Oxidation Tank Level, ft	17
Effluent Hold Tank Residence Time, min	9.1
Average Percent SO_2 Removal	96
Average Inlet SO_2 Concentration, ppm	2030
Percent Sulfite Oxidation in Effluent Hold Tank	54
Percent Sulfite Oxidation in Oxidation Tank	98
Air Stoichiometry, atoms oxygen/mole SO_2 absorbed	1.8
Oxidation Tank pH	4.8
Percent Limestone Utilization	88
Scrubber Inlet Liquor Gypsum Saturation, %	105
Oxidation Tank Liquor Gypsum Saturation, %	100
Centrifuge Cake Solids Content, wt %	79

Fly ash loading: High (2-7 grains/dry scf)
Slurry solids concentration: 15 percent
Oxidation tank level (7 ft diameter): 18 ft
Effluent hold tank level (20 ft diameter): 6.2 ft
Air flow to oxidizer: 220 scfm (for runs with forced oxidation)

Figure 5 shows the SO_2 removal as a function of adipic acid concentration and slurry flow rate for the TCA without spheres (grid tower). With a controlled limestone stoichiometry of 1.2 (5.6 to 6.1 scrubber inlet pH) and a slurry flow rate of 37 gpm/ft^2, adipic acid concentration greater than 2000 ppm would be required to achieve 90 percent SO_2 removal.

Figure 6 is similar to Figure 5 except that the data used for Figure 6 were obtained using 15 inches (5 inches per bed) of static height of spheres in the TCA. With a controlled limestone stoichiometry of 1.2, 90 percent SO_2 removal could be obtained with 2000 ppm adipic acid and only 19 gpm/ft^2 slurry flow rate, or with only 600 ppm adipic acid at 28 gpm/ft^2 slurry flow rate. With 37 gpm/ft^2, the required adipic acid concentration is only 300 ppm to achieve 90 percent removal. Both Figures 5 and 6 show that, at 1.2 limestone stoichiometry (5.6 to 6.1 scrubber inlet pH), SO_2 removal begins to "taper off" at about 600 ppm adipic acid concentration.

The effects of scrubber inlet pH and adipic acid concentration on SO_2 removal in the TCA are given in Figure 7. In comparing Figure 7 with Figures 5 and 6 (high pH data) at the same slurry flow rate of 28 gpm/ft^2, the low pH curves of Figure 7 have a noticeably steeper slope for adipic acid concentration above 600 ppm than is the case for the high pH data. At low pH, the adipic acid is partially ineffective because of a significant amount of un-ionized adipic acid. For example, Figure 6 shows that at a scrubber inlet pH of 5.6 to 6.1 and 28 gpm/ft^2, 75 percent SO_2 removal can be achieved without adipic acid. To achieve this same 75 percent removal, Figure 7 indicates that 600 ppm adipic acid is required at 5.3 scrubber inlet pH, and 1700 ppm at 4.6 inlet pH. Therefore, operation at a very low pH with adipic acid-enhanced limestone is not as attractive as at the higher pH from the process standpoint since adipic acid is only partially utilized for SO_2 scrubbing, and the SO_2 removal is far more sensitive to fluctuations in both pH and adipic acid concentration.

Figures 8 and 9 show the results of partial factorial limestone runs made on the spray tower. Common operating conditions for these runs were:

Fly ash loading: High (2-7 grains/dry scf)
Slurry solids concentration: 15 percent
Gas velocity: 9.4 ft/sec
Liquid-to-gas ratio: 85 gal/Mcf (2400 gpm)
Air flow to oxidizer: 250 scfm (for runs with forced oxidation)

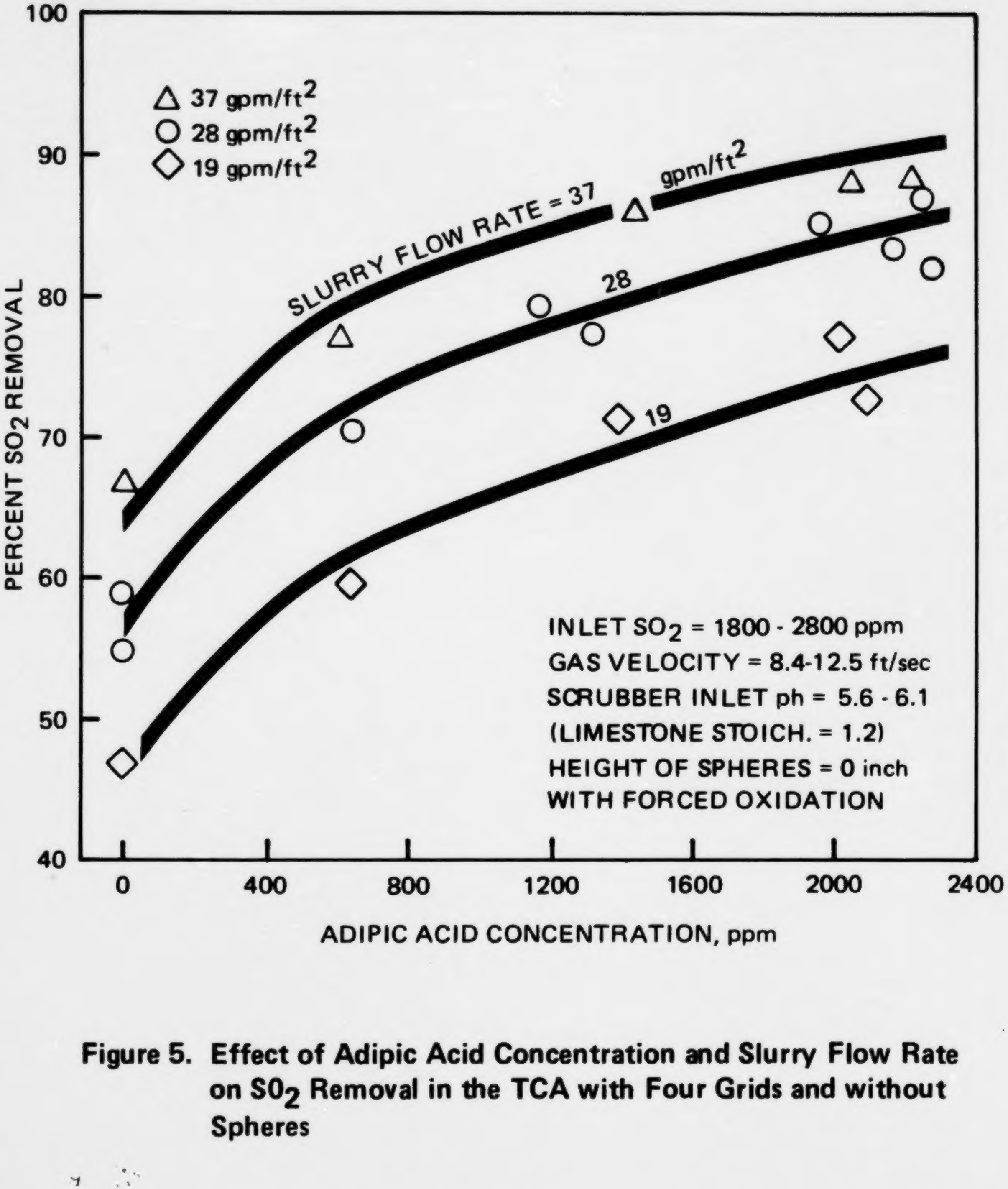


Figure 5. Effect of Adipic Acid Concentration and Slurry Flow Rate on SO_2 Removal in the TCA with Four Grids and without Spheres

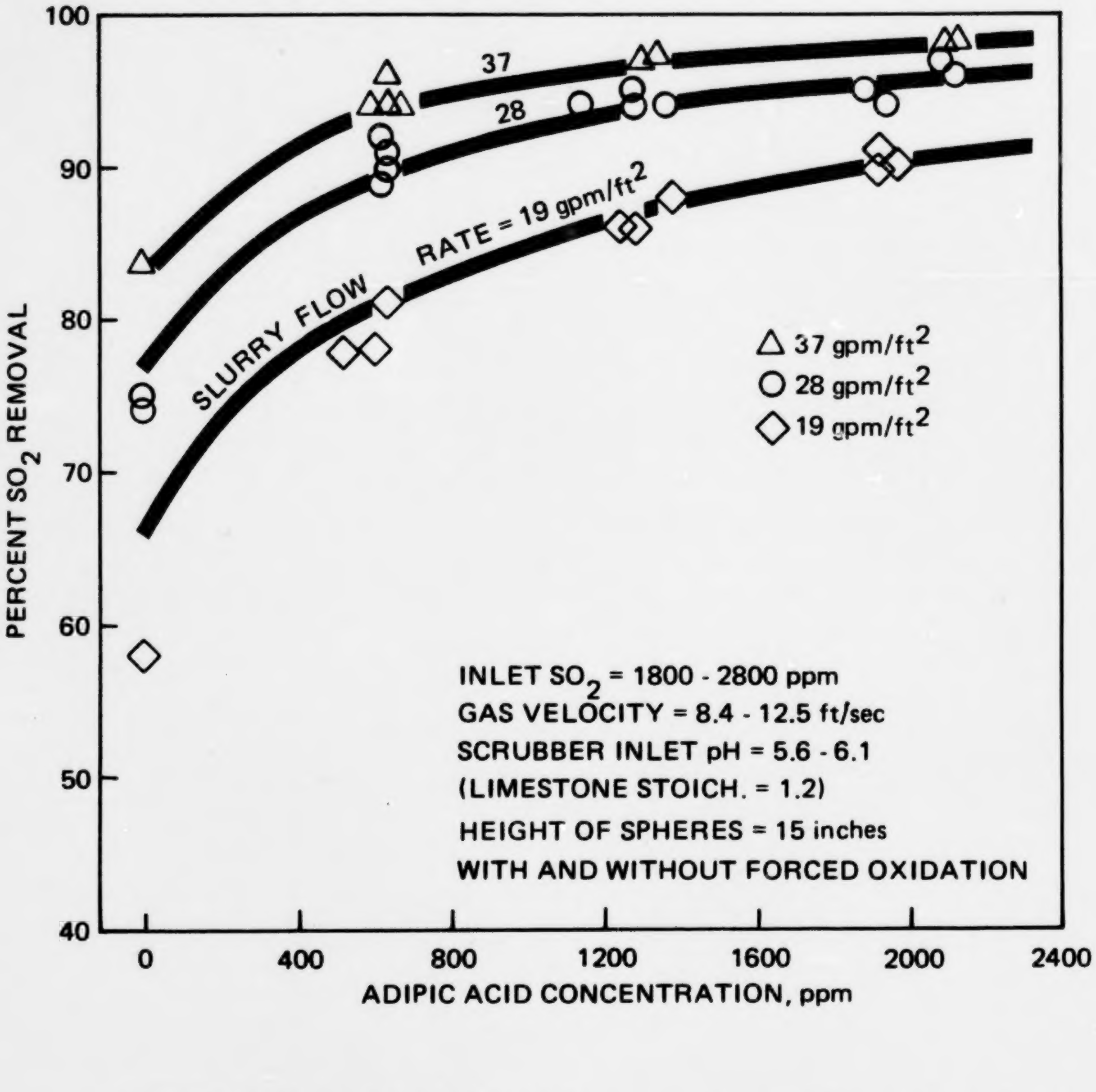


Figure 6. **Effect of Adipic Acid Concentration and Slurry Flow Rate on SO_2 Removal in the TCA with Four Grids and 15 inches of Spheres**

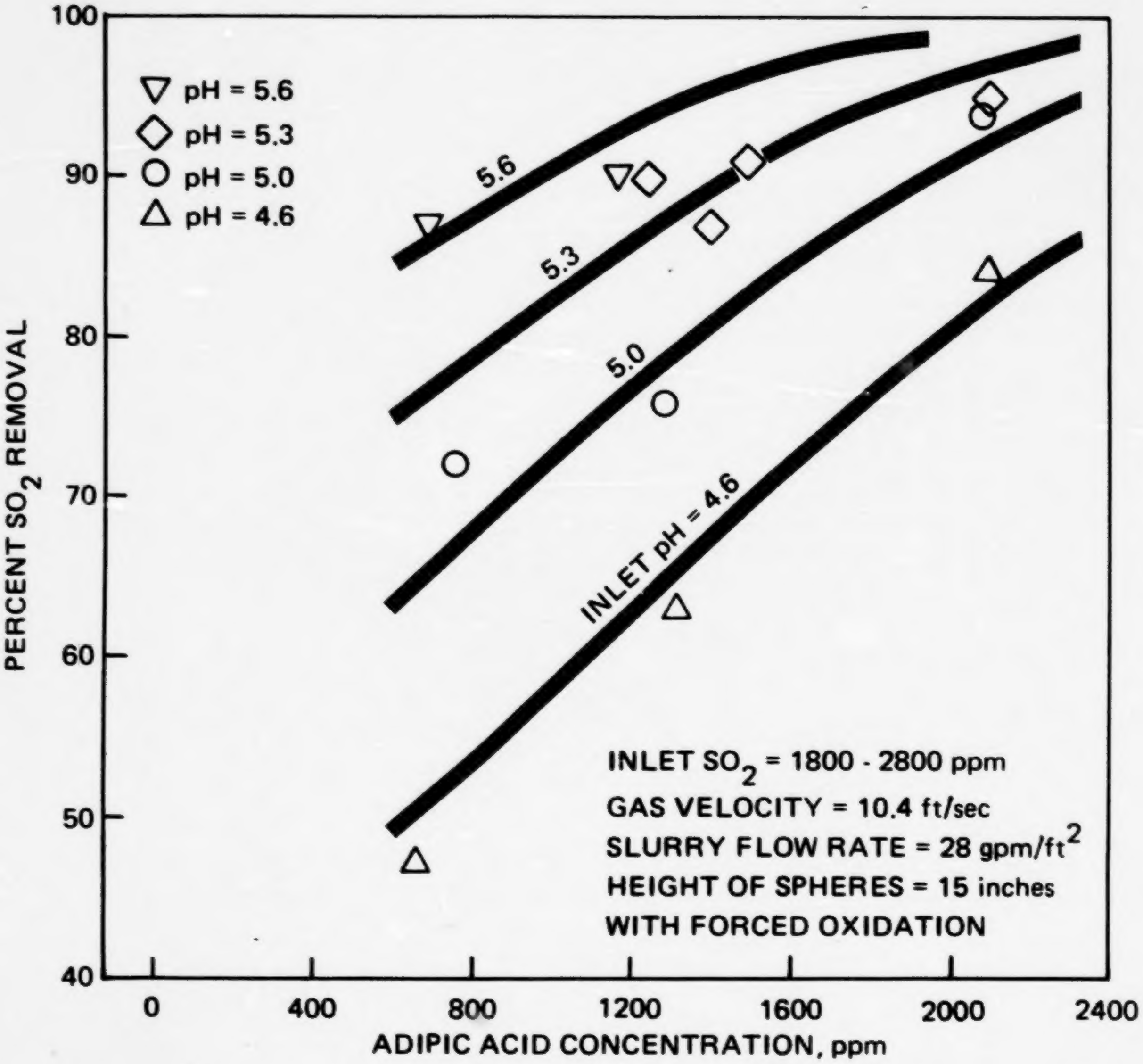


Figure 7. Effect of Adipic Acid Concentration and Scrubber Inlet pH on SO_2 Removal in the TCA with Four Grids and 15 Inches of Spheres

For runs without forced oxidation, a single effluent tank 20 ft in diameter with 8.5 ft tank level was used. For runs with forced oxidation, two tanks in series were used with an oxidation tank preceding the effluent hold tank. The oxidation tank was 8 ft in diameter with an 18-ft tank level.

Figure 8 gives the SO_2 removal as a function of adipic acid concentration and spray tower inlet pH for runs made without forced oxidation and at a constant liquid-to-gas ratio of 85 gal/Mcf. SO_2 removal is sensitive to both pH and adipic acid concentration within the ranges shown in the figure. At a liquid-to-gas ratio of 85 gal/Mcf, 90 percent SO_2 removal could be achieved at 5.4 scrubber inlet pH and 1200 ppm adipic acid, or 5.0 inlet pH and 2200 ppm adipic acid. At 4.6 inlet pH, the required adipic acid concentration is estimated to be in excess of 3000 ppm to yield 90 percent SO_2 removal.

Figure 9 shows the effects of scrubber inlet pH and adipic acid concentration on SO_2 removal for runs made with forced oxidation. As in Figure 8, the liquid-to-gas ratio was held constant at 85 gal/Mcf for the runs shown in Figure 9. By comparing the two figures, it is seen that forced oxidation dramatically improved the SO_2 removal, especially at the scrubber inlet pH below about 5.0. For example, at 1200 ppm adipic acid concentration and without forced oxidation, SO_2 removals were 59, 77, and 90 percent at a scrubber inlet pH of 4.6, 5.0, 5.4, respectively. The corresponding SO_2 removals with forced oxidation were 87, 91, and 94 percent.

The reason for improved SO_2 removal, particularly at low pH, is that forced oxidation eliminates bisulfite species, thereby reducing the SO_2 vapor pressure at the gas-liquid interface and improving the SO_2 mass transfer efficiency. This mechanism of improved SO_2 removal holds true when sulfite is not a major scrubbing species and the SO_2 removal does not depend on the sulfite-bisulfite buffer. In the case of Figures 8 and 9, calcium adipate is the major scrubbing reagent.

Therefore, it would be advantageous to operate a low pH, adipic acid-enhanced limestone or lime system with within-scrubber-loop forced oxidation which, in addition to improved SO_2 removal, requires low adipic acid makeup, minimizes gypsum scaling potential and produces a sludge with good disposal properties. Based on Figure 9, 90 percent SO_2 removal can be achieved at 5.0 inlet pH and only 1100 ppm adipic acid, or at 4.6 inlet pH with 1400 ppm adipic acid.

SPRINGFIELD FULL SCALE DEMONSTRATION

In August and September 1980, the EPA, through its contractor, Radian Corporation, conducted the first demonstration of the commer-

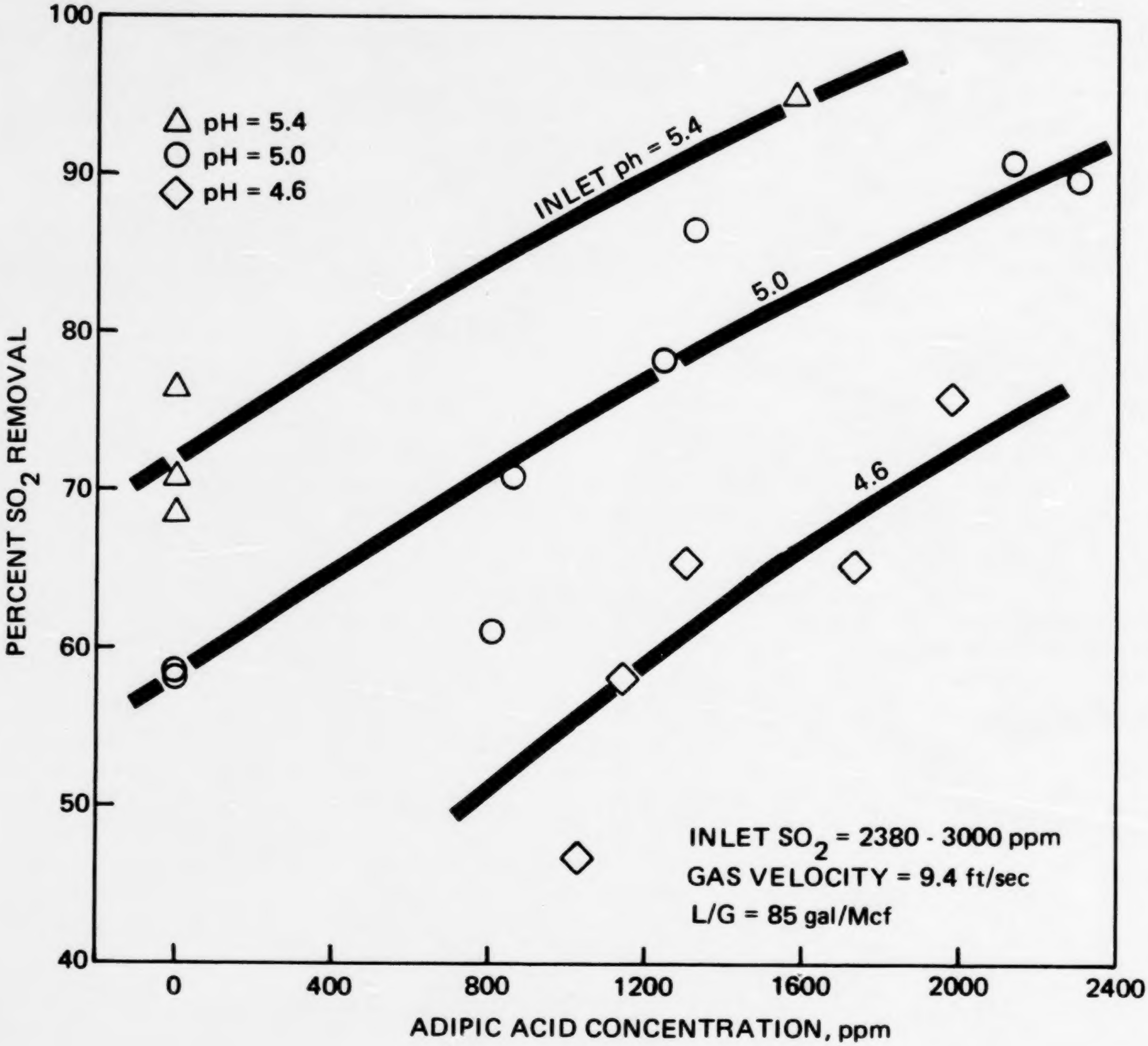


Figure 8. Effect of Adipic Acid Concentration and Scrubber Inlet pH on SO_2 Removal in the Spray Tower without Forced Oxidation

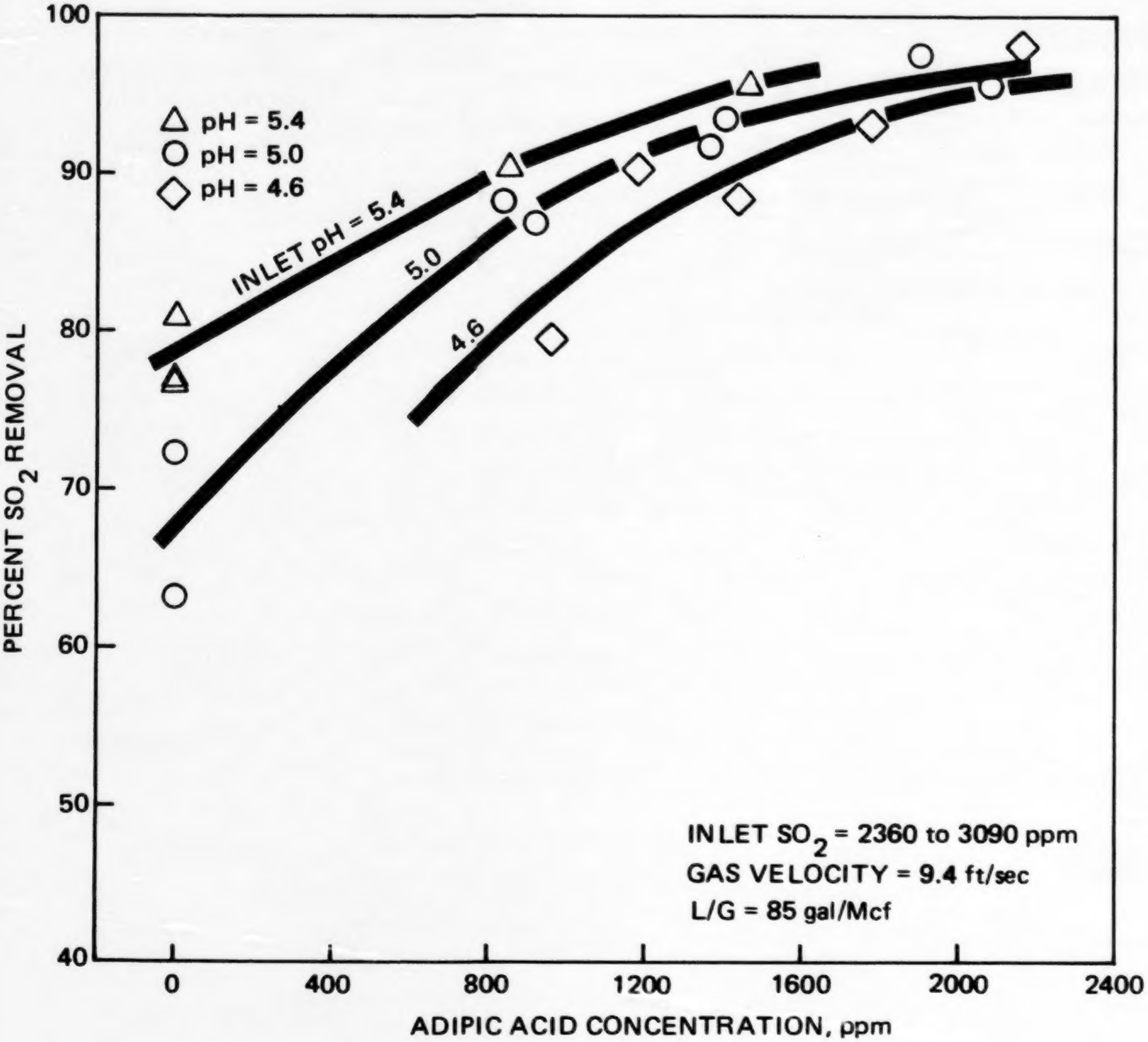


Figure 9. **Effect of Adipic Acid Concentration and Scrubber Inlet pH on SO_2 Removal in the Spray Tower with Forced Oxidation**

cial feasibility of adipic acid addition to a full scale limestone scrubber. The host facility was the Southwest Power Plant of the City Utilities of Springfield, Missouri. In that facility, 3.5 percent sulfur eastern coal is burned in two boilers with a total generating capacity of 200 MW. The flue gas from the electrostatic precipitators is scrubbed by two parallel 100 MW TCA's.

During this initial two month test period, seven different sets of test conditions were examined. Table 8 presents the major results of two baseline tests without adipic acid conducted on Modules S-1 and S-2, and seven tests with adipic acid conducted on Module S-1. All tests were without forced oxidation.

SO_2 removal improved from 68-72 percent for the baseline tests to 91, 95, and 96 percent with 840, 1040, and 1650 ppm adipic acid, respectively, at the same scrubber inlet pH of 5.5. At 5.0 inlet pH, SO_2 removal remained high at 84, 90, and 93 percent with 1250, 1300, and 1800 ppm adipic acid, respectively. At the lower pH of 5.0, the limestone utilization also increased from 76-84 percent for the baseline tests (pH 5.5) to 84-97 percent.

These results are consistent with the Shawnee findings. Furthermore, the SO_2 removal obtained at Springfield lay within 1 to 3 percentage points of model prediction based on the Shawnee data under similar operating conditions.

It should be noted that the odor associated with the adipic acid testing also was not a problem at Springfield.

Following these initial tests, the scrubber system was shut down for scheduled maintenance. Subsequently the demonstration continued with adipic acid testing both with and without forced oxidation. These results will be reported separately by others.

RICKENBACKER INDUSTRIAL BOILER DEMONSTRATION

In February, March, and April 1981, the EPA, through its contractor, PEDCo Environmental, Inc., conducted adipic acid-enhanced limestone scrubber tests on a industrial-sized system. The testing was carried out at the Rickenbacker Air Force Base on a Research-Cottrell/Bahco system rated at 55,000 scfm or about 27 MW equivalent. The tests, conducted with certified instrumentation, indicated an SO_2 removal efficiency increase from 55 percent without adipic acid, to 90 to 95 percent with adipic acid. This improvement was achieved at a scrubber inlet pH of 5.0 and adipic acid concentrations of between 2000 and 2500 ppm. More complete data will be reported separately by others.

Table 8

RESULTS OF SPRINGFIELD FULL-SCALE ADIPIC ACID DEMONSTRATION

Test	Gas Flow 10^3dscfm	Slurry Flow* gpm	Inlet SO_2 ppm dry	Scrubber Inlet pH	Adipic Acid Conc. ppm	Av. SO_2 Removal %	Limestone Util. %	Test Period hrs.
Baseline								
S-1	171	13,500	2410	5.5	0	68	76	497
S-2	163	13,500	2410	5.5	0	72	84	408
Adipic Acid (S-1)								
1	201	13,500	2460	5.5	840	91	82	122
2	187	13,500	2360	5.5	1040	95	75	50
3	190	13,500	2420	5.2	1000	88	94	74
4	193	13,500	2500	5.0	1250	84	91	44
5	192	13,500	2540	5.0	1800	93	84	33
6	196	13,500	2500	5.5	1650	96	73	89
7	175	13,500	2640	5.0	1300	90	97	84

* Slurry contains approximately 10 wt % solids.

5. ECONOMICS

The economics of limestone scrubbing, with or without additive, have been projected for forced oxidation systems designed to achieve an average of 90 percent SO_2 removal from high sulfur flue gas. The capital investment and revenue requirements are calculated using a Design Economics Computer Program which was jointly developed by TVA and Bechtel under EPA sponsorship.

For the purposes of this report, four cases have been studied, including a limestone case with MgO additive. The operating conditions for these cases are presented in Table 9. The evaluations are based on a 500 MW scrubbing facility incorporating forced oxidation and operating on flue gas from a boiler burning eastern coal containing 4 percent by weight sulfur. The cases evaluated are:

Case 1 - A limestone base case without additive operated at relatively high limestone stoichiometry and liquid-to-gas ratio to achieve 90 percent SO_2 removal. It should be noted that long term reliability with this mode of operation has not been demonstrated at Shawnee.

Case 2 - A limestone case with MgO addition. Oxidation of the scrubber bleed stream was chosen because in-loop oxidation is incompatible with magnesium-enhanced scrubbing. As in Case 1, long term reliability has not been demonstrated at Shawnee for this mode of operation.

Case 3 - A limestone case with adipic acid addition operated at high pH. Although only 800 ppm of adipic acid is required to obtain 90 percent SO_2 removal, degradation of adipic acid at high pH requires about five times the theoretical adipic acid addition rate.

Case 4 - A limestone case with adipic acid addition operated at low pH. For this case, 2000 ppm adipic acid is required. However, the low pH operation requires only 1.4 times the theoretical adipic acid addition rate and 1.05 limestone stoichiometry.

The results of the economic evaluations are presented in Tables 10 and 11. The capital investment and the first year revenue requirement in Table 10 include the dewatering equipment (thickener and filter) but exclude the waste sludge (filter cake) disposal area. Table 11 lists separately the first year revenue requirement for the waste sludge disposal area.

Table 9

CONDITIONS FOR ECONOMIC ANALYSIS OF LIMESTONE SCRUBBING WITH FORCED OXIDATION AND WITH OR WITHOUT ADDITIVE

Capacity:	500 MW
Coal:	4 wt % sulfur
Scrubber:	TCA with 3 beds, 4 grids, and 5 inches of static height of spheres per bed
SO_2 Removal Efficiency:	90%
Superficial Gas Velocity:	12.5 ft/sec
Number of Trains:	5, including one spare train
Solids Dewatering:	To 80% solids by thickener and rotary drum vacuum filter
Onstream Factor:	5500 hr/yr
Effluent Hold Tank Residence Time:	5 min
Oxidation Tank Residence Time:	5 min
Oxidation Tank Level:	18 ft
Air Sparger Pressure Drop:	5 psi
Oxidation Tank Agitator Hp:	0.002 brake Hp/gal
Solid Sulfite Oxidation:	99%
Air Stoichiometry:	1.7 lb-atoms O/lb mole SO_2 absorbed
Number of Tanks:	2 (effluent hold tank and oxidation tank)
Alkali:	Limestone

Case No.	1	2	3	4
Additive	-	MgO	Adipic Acid	Adipic Acid
Additive Concentration, ppm	-	5500 (a)	800	2000
Additive Rate, lb/hr	-	104	83.3 (b)	53.6 (c)
L/G, gal/Mcf	58	50	50	50
Limestone Stoichiometry, moles Ca/mole SO_2 absorbed	1.52	1.20	1.20	1.05
TCA Inlet pH	5.8	5.4	5.6	4.8
Mode of Oxidation	1 loop, 2 tanks	bleed stream	1 loop, 2 tanks	1 loop, 2 tanks

(a) Excess of molar equivalent of chloride.
(b) Five times theoretical consumption.
(c) 1.4 times theoretical consumption.

Table 10

RESULTS OF ECONOMIC ANALYSIS EXCLUDING WASTE SLUDGE DISPOSAL AREA

	Total Capital Investment			First Year Revenue Requirement		
Case No.	$MM(1982)	$/kW	Cost Factor	$MM(1984)	Mils/kWh	Cost Factor
1	87.40	174.8	1.000	25.01	9.09	1.000
2	85.26	170.5	0.975	24.15	8.78	0.966
3	83.97	167.9	0.961	24.01	8.73	0.960
4	83.22	166.4	0.952	23.56	8.57	0.942

Revenue requirement includes 14.7% annual capital charge.

Raw material costs (1984): Limestone - $8.5/ton
MgO - $460/ton
Adipic Acid - $1200/ton

Table 11

REVENUE REQUIREMENT IN WASTE SLUDGE DISPOSAL AREA

		First Year Revenue Requirement, Mils/kWh (1984)			
Case No.	Filter Cake, dry tons/hr	Total Excluding Sludge Disposal	Sludge Disposal	Total	Cost Factor
1	48.7	9.09	0.97	10.06	1.000
2	41.6	8.78	0.83	9.61	0.955
3	41.6	8.73	0.83	9.56	0.950
4	38.3	8.57	0.77	9.34	0.928

Revenue requirement includes 14.7% annual capital charges.
Sludge disposal cost assumes $10/dry ton, including 14.7% annual capital charges.

As shown in Table 10, both the total capital investment and the first year revenue requirement are the lowest for adipic acid-enhanced limestone scrubbing at low pH (Case 4). The total capital investment is reduced by 4.8 percent and the first year revenue requirement reduced by 5.8 percent for the limestone/adipic acid/low pH case (Case 4) compared with the conventional limestone case (Case 1). The revenue requirement includes 14.7 percent annual capital charge.

Total capital investment and operating costs for adipic acid-enhanced limestone at high pH (Case 3) are higher than those for limestone/adipic acid at low pH (Case 4), but are still lower than those for the conventional limestone (Case 1) or the limestone/MgO case (Case 2). Total capital investment is lower by 3.9 percent and the first year revenue requirement is lower by 4.0 percent for Case 3, compared with Case 1.

Table 11 illustrates the additional savings that result from adipic acid addition. Because of the lower pH operation, and thus lower limestone consumption, the amount of waste solids produced is lower for limestone/adipic acid cases (Cases 3 and 4) than for a limestone case (Case 1). Assuming a landfill disposal cost of $10/dry ton, including 14.7 percent annual capital charge, the first year revenue requirements for the sludge disposal area are 0.97, 0.83, and 0.77 mils/kWh for Cases 1,3, and 4, respectively. Thus, the total first year revenue requirement, including the sludge disposal area, is 9.34 mils/kWh for Case 4 compared with 10.06 mils/kWh for Case 1. This is a reduction of 7.2 percent, compared with 5.8 percent when the sludge disposal cost is not included.

These cost figures are cited as representative of typical scenarios only, and some variation from them would be normally expected. Moreover, the differences in total capital investments and operating costs between these cases are small. The principal conclusion from these evaluations is that adipic acid addition to a limestone scrubbing system decreases cost consistently when compared on the same basis.

It should also be noted that adipic acid use provides a level of flexibility in fuel and reagent choice and control level not available with other systems and in site-specific cases, may prove to be much more economically advantageous than indicated above.

ECONOMICS OF LIMESTONE FGD SYSTEMS USING ADIPIC ACID

Prepared by:

R. L. Torstrick, C. D. Stephenson, and J. D. Veitch
Division of Energy Demonstrations and Technology
Office of Power
Tennessee Valley Authority
Muscle Shoals, AL 35660

EPA Project Officer:

J. David Mobley
Industrial Environmental Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

Interagency Agreement No. 79DX0511

Presented at:

EPA's Industry Briefing on the
Adipic Acid Enhanced Limestone FGD Process

Springfield, MO
July 15, 1981

Preceding page blank

DISCLAIMER

This paper was prepared by the Tennessee Valley Authority and has been approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Tennessee Valley Authority or the U.S. Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

ECONOMICS OF LIMESTONE FGD SYSTEMS USING ADIPIC ACID

by

R. L. Torstrick, C. D. Stephenson, and J. D. Veitch
Division of Energy Demonstrations and Technology
Office of Power
Tennessee Valley Authority
Muscle Shoals, Alabama

ABSTRACT

The economics of the use of adipic acid additive in limestone FGD were examined using current design and economic premises established for the continuing series of economic evaluations performed by TVA for EPA. Economics were projected based on long-term Shawnee test facility operating data, Springfield test facility operating conditions, and recent Shawnee test facility operation. Incorporating the improved scrubbing efficiency effected by adipic acid into the design of a 90% SO_2 removal limestone FGD - landfill process reduces the capital investment and annual revenue requirements by about 2% each. A further similar reduction is attained using 95% removal and partial bypass. For existing facilities, based on Springfield and Shawnee data, using adipic acid increases capital investment and annual revenue requirements slightly but reduces the unit cost in terms of cost per ton of SO_2 removed. Although the differences in economics are not significant considering the accuracy of these cost projections the use of adipic acid for obtaining higher degrees of SO_2 removal may be significant in (1) bringing marginal plants into compliance, and (2) allowing power units to burn higher sulfur coals to reduce costs. One of the more significant advantages of using adipic acid is the ability to improve the SO_2 removal efficiency of an existing scrubber system simply by adding adipic acid.

INTRODUCTION

Recently TVA completed an economic evaluation of advanced concepts in limestone and lime FGD technology. The evaluation is part of a continuing program of utility FGD economic evaluations that TVA has conducted for EPA since 1967. In this case the evaluation is based on tests conducted at the EPA test facility at the TVA Shawnee Steam Plant near Paducah, Kentucky.

The Shawnee test facility originally consisted of three prototype-size scrubber units, each capable of processing about 30,000 aft^3/min (10 MW equivalent) of flue gas. One unit, a marble-bed absorber, was shut down in 1973 and converted to a cocurrent absorber in 1978. The other two units, a mobile-bed absorber (turbulent contact absorber or TCA) and a venturi-spray tower, have been operated under a variety of conditions since 1972. Until recently this test program was funded by EPA. It was operated by TVA with Bechtel National, Inc., serving as technical director for EPA. For the past ten years it has been used to develop and evaluate limestone and lime FGD technology (1). Using Shawnee test facility data, TVA and Bechtel developed a computer model that projects costs for full-sized limestone and lime FGD systems (2).

The computer model was used in this evaluation to calculate the economics of the numerous process variations that have been developed or evaluated at the Shawnee test facility. The results of the evaluation are being prepared and will be published by TVA and EPA.

A part of the evaluation dealt with the use of additives such as adipic acid to enhance the efficiency of limestone scrubbing slurries. The results for limestone processes with adipic acid are discussed in this paper.

The chemistry and practical aspects of organic acid buffers in limestone scrubbing FGD have been discussed by Hatfield, et al.(3), Rochelle (4), and Rochelle and King (5). The evaluation of adipic acid as such an additive, which was begun by EPA in 1978 and which constituted a major portion of the Shawnee test facility studies from 1978 to 1980, has been reported by Head and others (6) and Burbank and others (7).

From an economic standpoint, when incorporated into the design of new FGD systems, the use of adipic acid offers two possibilities for cost reductions. First, the improved SO_2 removal efficiency may permit the use of smaller or less complicated absorbers, lower L/G ratios, and lower stoichiometries. Also less limestone may be consumed and less waste may be produced. Second, the improved SO_2 removal efficiency may permit alternate designs, such as partial scrubbing and bypass, not adequate or practical with conventional limestone processes. Both of these possibilities are evaluated using current design and economic premises. Other economic benefits, such as upgrading the performance of existing units to avoid more costly alternatives were examined using design and operating data from the Springfield system and the Shawnee test facility.

DESIGN AND ECONOMIC PREMISES

The economic evaluations are based on FGD systems to meet the 1979 NSPS for a new 500-MW pulverized-coal-fired utility boiler. The FGD systems are designed with one redundant scrubber train, a redundant feed preparation train, 50% emergency flue gas bypass, and are costed as proven technology with no adjustments for estimated stage of development. The power plant is assumed to have a 30-year, 165,000-hour life and to operate 5,500 hours the first year. Flue gas compositions are based on a 3.5% sulfur, 15% ash, 11,700 Btu/lb eastern coal. A north-central location is used. Raw materials consist of limestone at \$8.50/ton and adipic acid at \$1,200/ton. The landfill or lined sludge pond waste disposal sites are one mile from the FGD facility.

The economics consist of capital investments in 1982 dollars, and first-year and levelized annual revenue requirements, both in 1984 dollars. The capital investments are based on major equipment costs developed from flow diagrams and material balances and factored costs for installation and ancillary equipment. First-year annual revenue requirements consist of raw material, operating, and overhead costs and levelized capital charges. In the levelized annual revenue requirements all costs are factored to account for a 10%/year discount for the cost of money and a 6%/year inflation rate for direct operating costs over the life of the power plant.

FGD conditions used are shown in Table 1. Four limestone process variations are compared.

Case 1: Full scrubbing at 90% removal with ponding
Case 2: Full scrubbing at 90% removal with forced oxidation and landfill
Case 3: Full scrubbing at 90% removal with adipic acid, forced oxidation, and landfill
Case 4: Partial scrubbing at 95% removal with adipic acid, forced oxidation, and landfill

RESULTS OF ECONOMIC EVALUATIONS PERFORMED BY TVA FOR EPA

Capital investments are shown in Table 2 and annual revenue requirements are shown in Table 3. Case 1, without adipic acid or forced oxidation and with pond disposal, presents costs of conventional limestone FGD. Case 2, also without adipic acid use, presents costs for a similar system, modified to include forced oxidation and landfill of FGD wastes as opposed to ponding of sludge. The adipic acid processes, cases 3 and 4, are directly comparable with case 2, including forced oxidation and landfill disposal, but reflecting the use of adipic acid.

TABLE 1. PROCESS DESIGN CONDITIONS AND PREMISES FOR ALTERNATIVE LIMESTONE SCRUBBING SYSTEMS DESIGNED FOR 90% SO_2 REMOVAL

	Limestone scrubbing alternative			
	Case 1[a]	Case 2[b]	Case 3[c]	Case 4[d]
Type of absorber	Spray tower	Spray tower	Spray tower	Spray tower
Inlet SO_2 concentration, ppm	2140	2140	2140	2140
Adipic acid concentration, ppm	-	-	1000	1700
Absorber gas velocity, ft/sec	10	10	10	10
SO_2 removal efficiency in scrubber, %	90	90	90	95
L/G, gal/kaft^3	90	90	80	95
Limestone stoichiometry, mols $CaCO_3$/mol SO_2 absorbed	1.3	1.3	1.2	1.1
Air stoichiometry, mols O/mol SO_2 absorbed	0	2.5	2.5	2.5
% sulfite oxidation	30	95	95	95
Filter cake solids, %	-	80	80	80
Pond settled solids, %	40	-	-	-
Bypass				
Emergency, % of scrubbed gas	50	50	50	50
Partial scrubbing, % of gas scrubbed	-	-	-	93.6
Reheat				
% from inline steam	100	100	100	77.7
% from bypassed gas	-	-	-	22.3

a. Full scrubbing at 90% removal and ponding.
b. Full scrubbing at 90% removal with forced oxidation and landfill.
c. Full scrubbing at 90% removal with adipic acid, forced oxidation, and landfill.
d. Partial scrubbing at 95% removal with adipic acid, forced oxidation, and landfill.

TABLE 2. CONVENTIONAL AND ADVANCED LIMESTONE SCRUBBING PROCESSES

CAPITAL INVESTMENT

	Capital investment, k$			
	Case 1[a]	Case 2[b]	Case 3[c]	Case 4[d]
Direct Investment				
Material handling	2,518	2,518	2,556	2,542
Feed preparation	4,618	4,618	4,590	4,383
Gas handling	11,246	11,642	11,479	11,165
SO_2 absorption	19,327	19,327	18,550	18,795
Oxidation	-	2,118	2,090	2,125
Reheat	3,844	3,844	3,844	3,462
Solids disposal	2,126	3,352	3,340	3,290
Total	43,679	47,419	46,449	45,762
Services, utilities, and miscellaneous	2,621	2,845	2,787	2,746
Total	46,300	50,264	49,236	48,508
Landfill or pond construction	14,644	2,195	2,041	1,900
Landfill equipment	-	609	585	560
Total	60,944	53,068	51,862	50,968
Indirect Investment				
Engineering design and supervision	3,241	3,518	3,447	3,396
Architect and engineering contractor	926	1,005	985	970
Construction expense	7,408	8,042	7,878	7,761
Contractor fees	2,315	2,513	2,462	2,425
Contingency	6,019	6,534	6,401	6,306
Waste disposal	4,042	1,098	1,021	950
Total fixed investment	84,895	75,778	74,056	72,776
Other Capital Investment				
Allowance for startup and modifications	5,297	5,750	5,633	5,549
Interest during construction	13,244	11,727	11,462	11,266
Land	1,890	661	621	601
Working capital	3,255	3,169	3,108	3,026
Total capital investment	108,581	97,085	94,880	93,218
$/kW	217	194	190	186

a. Full scrubbing at 90% removal and ponding.

b. Full scrubbing at 90% removal with forced oxidation and landfill.

c. Full scrubbing at 90% removal with adipic acid, forced oxidation, and landfill.

d. Partial scrubbing at 95% removal with adipic acid, forced oxidation, and landfill.

Basis: North central new power unit with 30-year life at 5500 hr/yr full-load operation.

Mid-1982 costs, 1 spare absorber train, and provisions for emergency bypass of 50% of the scrubbed gas.

Reheat to 175°F as required.

Capital costs begin with an inlet plenum downstream of the ESP.

Stack plenum and stack excluded.

Disposal site one-mile from power plant.

TABLE 3. CONVENTIONAL AND ADVANCED LIMESTONE SCRUBBING PROCESSES

ANNUAL REVENUE REQUIREMENTS

	Annual cost, k$			
	Case 1[a]	Case 2[b]	Case 3[c]	Case 4[d]
Direct Costs - First Year				
Raw materials				
Limestone	1,128	1,128	1,041	953
Adipic acid	-	-	169	272
Total raw materials cost	1,128	1,128	1,210	1,225
Conversion costs				
Operating labor and supervision				
FGD	460	658	658	644
Solids disposal	-	543	531	516
Utilities				
Process water	35	26	26	24
Electricity	1,723	2,005	1,864	1,917
Steam	1,365	1,365	1,367	1,062
Fuel	-	211	201	190
Maintenance				
Labor and material	4,143	4,038	3,956	3,898
Analyses	104	104	104	70
Total conversion costs	7,831	8,950	8,707	8,321
Total direct costs	8,959	10,078	9,917	9,546
Indirect Costs - First Year				
Overheads				
Plant and administrative (60% of conversion costs less utilities)	2,824	3,016	2,963	2,894
Total first-year operating and maintenance costs	11,783	13,094	12,879	12,440
Levelized capital charges (14.7% of total capital investment)	15,961	14,271	13,947	13,703
Total first-year annual revenue requirements	27,744	27,366	26,827	26,143
Levelized first-year operating and maintenance costs (1.886 x first-year O and M)	22,222	24,696	24,291	23,460
Levelized capital charges (14.7% of total capital investment)	15,961	14,271	13,947	13,703
Levelized annual revenue requirements	38,183	38,967	38,238	37,163
	Mills/kWh			
First-year annual revenue requirements	10.09	9.95	9.76	9.51
Levelized annual revenue requirements	13.89	14.17	13.90	13.51

a. Full scrubbing at 90% removal and ponding.
b. Full scrubbing at 90% removal with forced oxidation and landfill.
c. Full scrubbing at 90% removal with adipic acid, forced oxidation, and landfill.
d. Partial scrubbing at 95% removal with adipic acid, forced oxidation, and landfill.

Basis: One-year, 5500-hour operation of system as described in capital investment table.

Mid-1984 cost basis.

The results indicate that capital investment is highest for case 1 because the investment for the disposal pond is greater than the investment for landfills. Design for forced oxidation - landfill (case 2) in comparison with onsite ponding (case 1) reduces capital investment about 10% ($23/kW). In case 3, the use of adipic acid reduces the capital investment about 2% ($4/kW) compared with the otherwise identical case 2 process. The effect results from the increased SO_2 removal efficiency which reduces the absorber size and the absorbent pumping requirements. Increasing the removal efficiency to 95% and bypassing a portion of the flue gas (case 4) further decreases capital investment by about 2%. Most of this reduction is a result of improved absorbent utilization and reduced reheat requirements.

First-year annual revenue requirements for forced oxidation - landfill (case 2) are slightly lower (.14 mills/kWh) than those for onsite ponding (case 1). First-year annual revenue requirements for the forced-oxidation alternative are further reduced (.19 mills/kWh) by using adipic acid (case 3). The largest cost reduction is in electricity use because of the lower pumping requirements. A further reduction (.25 mills/kWh) is attained by use of 95% SO_2 removal and partial bypass (case 4). In this case the saving is largely reheat steam.

In both cases 3 and 4 using adipic acid, the capital investment and annual revenue requirements associated with adipic acid addition are minimal. Capital investment for adipic acid storage, handling, and addition are more than compensated for by the reduced capital investment for the limestone handling and feed preparation areas. Raw material costs for adipic acid are no more than 1% of the total annual revenue requirements and again are partially compensated for by lower absorbent requirements.

Comparisons using levelized annual revenue requirements (in which the operating and maintenance costs, as well as, the capital charges are levelized for a 6%/year inflation and 10%/year cost of money) show the same general relationships. However, the levelized annual revenue requirements for case 1 are relatively less because pond disposal has lower operating and maintenance costs, and thus there is less difference between first-year and levelized annual revenue requirements.

Cost differences of these magnitudes would not normally be regarded as highly significant in cost studies of this type. The processes are very similar except for the use of additives. Excluding extreme variations in additive cost (relative to other cost variations) the well-documented improvements in absorbent utilization and SO_2 removal efficiency indicate that additives provide a real, if small, cost advantage for high-sulfur coal landfill processes designed for a particular SO_2 removal efficiency. Adipic acid also permits the use of partial bypass, which further reduces costs.

Although cost data are not presented here, other results in the study from which these data were derived have shown that the annual revenue requirements of processes using additives and pond disposal are higher than those of the same process without additives because of the additive lost in the low-solids wastes and the cost for additional protection against seepage in the pond. The cost of the additive in these cases is approximately the same as the limestone cost. The overall increase in annual revenue requirements is minor, however.

PROJECTED DESIGN AND ECONOMICS BASED ON RESULTS AT SPRINGFIELD

One of the more significant advantages of using adipic acid is the ability to improve the SO_2 removal efficiency of an existing scrubber system simply by adding adipic acid. To demonstrate the buffering effect of adipic acid, the full-scale 194-MW TCA on unit No. 1 at Springfield was operated using pH control at 5.0-5.4 without adipic addition. During this test, the SO_2 removal efficiency averaged about 58%. Adipic acid was then added to the limestone hold tank to a concentration of about 2000 ppm. Following the addition of adipic acid, while controlling the pH in the range of 5.0-5.4, efficiency for the TCA-single hold tank, forced-oxidation system increased from about 58% to 90%. Increasing the adipic acid concentration to 3000 ppm further increased the SO_2 removal efficiency to 95%. Table 4 shows the scrubber operating conditions that were used during these forced oxidation tests. Using the operating conditions in Table 4 for the Springfield facility, capital investment and annual revenue requirements for a 194-MW unit burning 3.9% sulfur coal were projected in the same manner as those shown in Tables 2 and 3. The results are shown in Table 5.

Although both the capital investment and first-year annual revenue requirements increase with increasing adipic acid concentration, the cost per unit of SO_2 removed decreases as adipic acid concentrations increase.

COMPARATIVE TCA PROCESS DESIGN AND ECONOMICS BASED ON TEST RESULTS AT SHAWNEE

For comparison with the design and economics based on the Springfield conditions, design and economics for a 194-MW TCA process based on the results at Shawnee were also projected. Table 6 shows the process design conditions used for this analysis. The projected economics are shown in Table 7. These results for cases 1 and 2 indicate that investment and first-year revenue requirements increase with increasing SO_2 removal efficiencies. However, unit costs per ton of SO_2 removed decrease. Case 3 shows a slight advantage for operating with a two-tank forced-oxidation mode, over the single-tank mode shown in case 1.

Although the magnitude of the results differ slightly from those based on the Springfield conditions, the results are similar. In both comparisons, because of the improved SO_2 removal efficiencies attainable with the addition of adipic acid, the unit cost for SO_2 removal decreases.

CONCLUSIONS

Based on the current design and economic premises, the use of adipic acid decreases capital investment and annual revenue requirements by about 2% each when the improved SO_2 removal achieved with adipic acid is incorporated into the design of the FGD system. An additional decrease of the same general magnitude is attained by using adipic acid at 95% SO_2 removal with partial bypass.

TABLE 4. PROCESS DESIGN CONDITIONS AND RESULTING SO_2 REMOVAL EFFICIENCIES ATTAINED AT SPRINGFIELD

	Limestone scrubbing alternative		
	Case 1	Case 2	Case 3
Type of absorber	TCA	TCA	TCA
Inlet SO_2 concentration, ppm	2,500	2,500	2,500
Adipic acid concentration, ppm	-	2,000	3,000
SO_2 removal efficiency in scrubber, %	58	90	95
L/G, gal/kaft^3	60	60	60
Limestone stoichiometry, mols $CaCO_3$/ mol SO_2 absorbed	1.1	1.1	1.1
pH	5.0-5.4	5.0-5.4	5.0-5.4

TABLE 5. COMPARATIVE ECONOMICS FOR 194-MEGAWATT LIMESTONE SCRUBBING SYSTEMS BASED ON PROCESS DESIGN CONDITIONS AT SPRINGFIELD[a]

	Limestone scrubbing alternative		
	Case 1	Case 2	Case 3
Adipic acid concentration, ppm	-	2,000	3,000
SO_2 removal efficiency, %	58	90	95
Total capital investment[a]			
$k	34,266	36,106	36,175
$/kW	177	186	187
Total first year annual revenue requirements			
$k	10,224	11,222	11,364
Mills/kWh	9.6	10.5	10.7
$/ton SO_2 removed	600	424	407

[a] Does not include spare scrubber.

TABLE 6. PROCESS DESIGN CONDITIONS FOR 194-MEGAWATT LIMESTONE SCRUBBING SYSTEMS BASED ON RESULTS AT SHAWNEE

	Limestone scrubbing alternative		
	Case 1	Case 2	Case 3
Type of absorber	TCA	TCA	TCA
Inlet SO_2 concentration, ppm	2,500	2,500	2,500
Adipic acid concentration, ppm	2,000	2,000	2,200
SO_2 removal efficiency in scrubber, %	90	95	95
L/G, gal/kaft^3	45	50	45
Limestone stoichiometry, mols $CaCO_3$/ mol SO_2 absorbed	1.1	1.1	1.1
pH	5.1	5.1	5.1
Scrubber redundancy	0	0	0
Number of tanks	1	1	2

TABLE 7. COMPARATIVE ECONOMICS FOR 194-MEGAWATT LIMESTONE SCRUBBING SYSTEMS BASED ON RESULTS AT SHAWNEE

	Limestone scrubbing alternative		
	Case 1	Case 2	Case 3
Adipic acid concentration, ppm	2,000	2,000	2,200
SO_2 removal efficiency, %	90	95	95
Total capital investment			
\$k	34,894	35,585	35,108
\$/kW	180	183	181
Total first year annual revenue requirements			
\$k	10,727	10,963	10,836
Mills/kWh	10.1	10.3	10.2
\$/ton SO_2 removed	405	392	388

Costs associated with adipic acid addition are small and more than compensated for by improved absorbent utilization and reduced pumping costs.

Costs projected on the same basis using Springfield design data show a slight increase in capital investment and a 10% increase in annual revenue requirements with adipic acid use. The increase in SO_2 removal from 58% to 90%-95% results in about a 30% decrease in terms of cost per ton of SO_2 removed. A similar projection using results obtained at the Shawnee test facility shows similar results.

More important than the slight reduction in costs for adipic acid in comparison to nonadipic acid systems is the ability of these systems to improve SO_2 removal capability. Thus the use of adipic acid can be effective in ensuring that SO_2 removal efficiencies can be achieved, particularly for existing systems currently attaining marginal degrees of SO_2 removal. Adipic acid systems thus may provide ease in meeting the 30-day rolling average SO_2 standards and provide a cushion for burning coals with varying sulfur content.

REFERENCES

1. D. A. Burbank and S. C. Wang, 1980, EPA Alkali Scrubbing Test Facility: Advanced Program - Final Report (October 1974-June 1978), EPA-600/7-80-115, U.S. Environmental Protection Agency, Washington, D.C.

2. W. L. Anders and R. L. Torstrick, 1981, Computerized Shawnee Lime/Limestone Scrubbing Model Users Manual, EPA-600/8-81-008, U.S. Environmental Protection Agency, Washington, D.C.

3. J. D. Hatfield, Y. K. Kim, and R. C. Mullins, 1972, Sulfur Oxide Removal from Power Plant Stack Gas - Study of the Effect of Organic Acids on the Wet-Limestone Scrubbing Process, TVA Special Report No. 458, prepared for EPA under contract No. TV-34425A, February 24, 1972.

4. G. T. Rochelle, 1977, Process Synthesis and Innovation in Flue Gas Desulfurization, Ph. D. Disseration, University of California at Berkeley.

5. G. T. Rochelle and C. J. King, 1977, The Effect of Additives on Mass Transfer in $CaCO_3$ or CaO Slurry Scrubbing of SO_2 from Waste Gases, Industrial and Engineering Chemistry, Fundamental, Vol. 16, No. 1, pp. 67-75.

6. H. N. Head, S. C. Wang, D. T. Rabb, R. H. Borgwardt, J. E. Williams, and M. A. Maxwell, 1979, Recent Results from EPA's Lime/Limestone Scrubbing Programs - Adipic Acid as a Scrubber Additive, In: Proceedings: Symposium on Flue Gas Desulfurization - Las Vegas, Nevada, March 1979, Vol. 1, EPA-600/7-79, U.S. Environmental Protection Agency, Washington, D.C., pp. 342-385.

7. D. A. Burbank, S. C. Wang, R. R. McKinsey, and J. E. Williams, 1980, Test Results on Adipic Acid - Enhanced Limestone Scrubbing at the EPA Shawnee Test Facility - Third Report - preprint of paper presented at the Sixth EPA Symposium on Flue Gas Desulfurization, Houston, Texas, October 28-31, 1980.

APPENDIX

Attendees

Industry Briefing on Adipic Acid Enhanced Limestone Flue Gas Desulfurization Process

July 15, 1981

Attendee List

Altin, Charles
Ebasco Services, Inc.
145 Technology Park/Atlanta
Norcross, GA 30092

Antonetti, Jeffrey O.
Indianapolis Power & Light Co.
P. O. Box 1595B
Indianapolis, IN 46206

Bakke, Even
Peabody Process Systems, Inc.
835 Hope St.
Stamford, CT 06907

Bentley, Royce
Public Service of Oklahoma
P. O. Box 201
Tulsa, OK 74102

Bitler, John A.
General Battery Corporation
P. O. Box 1262
Reading, PA 19603

Bjorklun, Stephen A.
Burns & McDonnell Engineering
P. O. Box 173
Kansas City, MO 64141

Blann, Dale R.
Acurex Corporation
Route 1, Box 423
Morrisville, NC 27560

Boucher, James E.
Gibbs & Hill, Inc.
8420 West Dodge Rd.
Omaha, Nebraska 68114

Boward, Willard
FMC Corporation
231 N. Martingale Rd.
Schaumburg, IL 60194

Brenner, Harold R.
Monsanto
800 North Lindbergh Blvd.
St. Louis, MO 63166

Boscak, Vladimir
GE Environmental Services
One Penn Plaza
New York, NY 10001

Burbank, Dewey A.
Bechtel National, Inc.
P. O. Box 3965
San Francisco, CA 94119

Buschmann, John C.
Niro Atomizer
9165 Rumsey Rd.
Columbia, MD 21045

Byrne, Robert E.
Research-Cottrell
P. O. Box 1500
Somerville, NJ 08876

Campbell, Ivor
Clyde Williams & Co.
160 East Broad St.
Columbia, OH

Chang, John
Acurex Corporation
Route 1, Box 423
Morrisville, NC 27511

Chi, C. T.
Monsanto
P. O. Box 12839
Pensacola, FL 32575

Cho, Hyun Je
T. D. Williamson, Inc.
P. O. Box 3409
Tulsa, OK 74101

Ciliberto, Darryl
Tampa Electric Co.
P. O. Box 111
Tampa, FL 33601

Clark, David R.
Allied Fibers & Plastics
8170 Corporate Park Drive
Cincinnati, OH 45242

Colley, David
Radian Corporation
P. O. Box 9948
Austin, TX 78766

Corinthios, Hanna
Ontario Ministry of
Environment
Air Resources Branch
Toronto, Ontario
CANADA

Cunic, John

Darrough, Earl H.
High Technology Materials Division
Cabot Corporation
1020 Park Avenue
Kokomo, IN 46901

Davis, Richard L.
Koppers Co., Inc.
2701 Koppers Bldg.
Pittsburgh, PA 15219

Davis, S.A.
U.S. Steel Corporation
600 Grant St.
Pittsburgh, PA 15230

Dempsey, J. Herbert
Acurex Corporation
Route 1, Box 423
Morrisville, NC 27511

Dickerman, Jim
Radian Corporation
P. O. Box 9948
Austin, TX 78766

Doctor, Richard D.
Argonne National Laboratory
9700 South Cass
Bldg. 362-C205
Argonne, IL 60439

Douglas, Robert E.
Conoco Coal Development Co.
Research Division
Library, PA 15120

Downs, William
Babcock & Wilcox
1562 Beeson St.
Alliance, OH 44601

Drabkin, Marvin
Mitre Corporation
1820 Dolley Madison Blvd.
McLean, VA 22102

DuBois, Michael J.
Commonwealth Edison
P. O. Box 767
Chicago, IL 60690

Fassnacht, J. H.
E. I. DuPont De Nemours & Co.
451 Beverly Place
Lake Forest, IL 60045

Fraley, Dave (Springfield City Ute)

Fortune, Owen F.
General Electric
Environmental Services, Inc.
200 North Seventh St.
Lebanon, PA 17042

Frabotta, Dante
Environmental Systems Division
Combustion Engineering, Inc.
P. O. Box 43030
31 Inverness Center Pkwy.
Birmingham, AL 35243

Gaynor, John
United States Gypsum Co.
1000 East Northwest Highway
Des Plaines, IL 60016

Gibson, Elizabeth
Radian Corporation
40 Broad Street
Suite 820
Boston, MA 02109

Glover, Rob
Radian Corporation
P. O. Box 9948
Austin, TX 78766

Gupta, Vir
Illinois Environmental
  Protection Agency
2200 Churchill St.
Springfield, IL 62706

Haider, Oazi
Industrial Generating Company
P. O. Box 1111
Rockdale, TX 76567

Hawkins, J.A.
Ebasco Services, Inc.
145 Technology Park/Atlanta
Norcross, GA 39902

Hargrove, Buddy
Radian Corporation
P. O. Box 9948
Austin, TX 78766

Hengel, Jim
Black & Veatch
P. O. Box 8405
Kansas City, MO 64114

Henzel, David
PEDCo Environmental, Inc.
Chester Towers
11499 Chester Rd.
Cincinnati, OH 45246

Hess, William R.
E. I. duPont de Nemours & Co.
1007 Market St.
PD, N9451
Wilmington, DE 19898

Hicks, N. Dale
City Utilities of Springfield
Southwest Power Plant
301 E. Central Street
Springfield, MO 65801

Hughey, John E.
Zurn-Air Systems Division
P. O. Box 2206
Birmingham, AL 35201

Iyer, Ramani
G.E. Environmental Services, Inc.
1 Penn Plaza
New York, NY 10001

Jenkins, Stephen D.
Tampa Electric Company
P. O. Box 111
Tampa, FL 33601

Johnston, C.W.
Badische Corporation
602 Copper Rd.
Freeport, TX 77541

Joos, David
Black & Veatch
P. O. Box 8405
Kansas City, MO 64114

Josephs, D.
American Air Filter
P. O. Box 35690
Louisville, KY 40232

Kaplan, Marilyn
McIlvaine Company
2970 Maria Ave.
Northbrook, IL 60062

Kar, Pat

Keen, Robert T.
Bechtel Power Corporation
520 South Post Oak Rd.
Houston, TX 77001

Kinkhabwala, Minesh
Thyssen-CEA Environmental Systems, Inc.
555 Madison Ave.
New York, NY 10022

Lowell, Phil
P.S. Lowell & Co., Inc.
4107 Medical Parkway
Suite 214
Austin, TX 78756

Mack, Stan
Apollo Technologies
1 Apollo Drive
Whippany, NJ

Maxwell, Michael A.
U.S. EPA
MD-61
RTP, NC 27711

McCarthy, Bill
RD 681
U.S. EPA
401 M St., SW
Washington, DC 20460

Meyler, James A.
Joy Manufacturing Co.
Western Precipitation Division
P. O. Box 2744, Terminal Annex
Los Angeles, CA 90051

Miller, James F.
Battelle Columbus Laboratories
505 King Avenue, Rm 6333
Columbus, OH 43201

Miller, Robert F.
Cabot Corporation
RFD3, Birch Ridge Dr.
Burlington, CT 06013

Mobley, J. David
U.S. EPA
MD-61
RTP, NC 27711

Mobrey, David S.
Allied Corporation
1411 Broadway
New York, NY 10018

Murad, Frederick
Thyssen-CEA Environmental Systems, Inc.
555 Madison Avenue
New York, NY 10022

Muren, Edward J.
Research-Cottrell, Inc.
222 South Riverside Plaza
Chicago, IL 60606

Myers, Stephen D.
Bird Machine Co., Inc.
1580 N. Northwest Highway
Suite 116
Park Ridge, IL 60068

Nolen, Paul
UOP - Air Correction Division
101 Merritt 7, Box 5440
Norwalk, CT 06856

Ostroff, Norman
Peabody Process Systems, Inc.
835 Hope Street
Stamford, CT 06907

Nauyen, Y.V.

Oven, Joe E.
Commonwealth Associates, Inc.
209 East Washington Ave.
Jackson, MI 49201

Oxley, J. H.
Battelle Columbus Laboratories
Room 10-222
505 King Ave.
Columbus, OH 43201

Papajewski, Knut
Thyssen-CEA Environmental Systems, Inc.
555 Madison Ave.
New York, NY 10022

Parekh, R.
Dorr-Oliver, Inc.
274 Riverside Ave.
Westport, CT 06880

Pasha, M.
American Air Filter
P. O. box 35690
Louisville, KY 40232

Crocker, D. N.
Amax Coal Company
105 South Meridian
Indianapolis, IN 46225

Pfeffer, Steven J.
UOP - Air Correction Division
101 Merritt 7
Norwalk, CT 06856

Pilgrim, Jim
Tennessee Valley Authority
400 Corroon Rd. & Black Bldg.
Chattanooga, TN 37401

Raduta, Margaret C.
IU Conversion Systems, Inc.
115 Gibraltar Rd.
Horsham, PA 19044

Reddy, K.R.
Institute of Natural Resources
325 West Adams
Springfield, IL 62706

Richardson, P. M.
E. I. duPont de Nemours & Co.
1007 Market St.
PD, N6502
Wilmington, DL 19898

Rochelle, Gary
University of Texas
Department of Chemical Engineering
Austin, TX 78712

Rowland, Clyde H.
M. W. Kellogg
16200 Park Row
Industrial Park 10
Houston, TX 77084

Ruggeri, Sam
American Electric Power Service Corp.
P. O. Box 487
Canton, OH 44701

Sarmiento, Otto
UOP - Air Correction Division
101 Merritt 7
Norwalk, CT 06856

Schafferman, Dale
Missouri Division of Energy
Box 176
Jefferson City, MO 65102

Schulz, David
U.S. EPA
Region V
230 South Dearborn St.
Chicago, IL 60604

Shattuck, Don
Stearns-Roger Engineering Corp.
P. O. Box 5888
Denver, CO 80217

Shroff, G.
Bechtel Power Corporation
15740 Shady Grove Rd.
Gaithersburg, MD 20760

Silence, William L.
Cabot Corporation
1020 Park Avenue
Kokomo, IN 46901

Molenski, John V.

Spring, Richard A.
Kansas City Power & Light
LaCygne, KS 66040

Statnick Bob
RD 681 (OEET)
U.S. EPA
401 M St., S.W.
Washington, DC 20460

Stensland, John G.
FMC Corporation
231 North Martingale Rd.
Schaumburg, IL 60194

Stewart, Jack F.
Babcock & Wilcox
20 South Van Buren Ave.
Barberton, OH 44203

Stone, Bruce T.
City Utilities of Springfield
301 East Central
Springfield, MO 65802

Stopek, David J.
Science Applications, Inc.
Chestnut Ridge Rd.
Chestnut Ridge Prof. Bldg. #8
Morgantown, WV 26505

Straw, Harry A.
E. I. duPont de Nemours & Co.
1007 Market St.
PD, N9451
Wilmington, DE 19898

Sullivan, Jerry
Public Service of Indiana
1000 East Main
Plainfield, IN 46128

Swanson, Carl E.
Newmont Exploration Ltd.
P. O. Box 310
Danbury, CT 06810

Torstrick, Robert L.
Tennessee Valley Authority
501 Chemical Engineering Bldg.
Muscle Shoals, AL 35660

Valkiunas, John J.
Ecolaire Environmental Co.
120 W. Golf Rd.
Suite 114
Schaumburg, IL 60195

Van Ness, Robert P.
Louisville Gas & Electric Co.
P. O. Box 32010
Louisville, KY 40232

Weinrich, Stanley
International Paper Co.
P. O. Box 797
Tuxedo Park, NY 10987

Wells, R. Murray
Radian Corporation
P. O. Box 9948
Austin, TX 78766

Wild, Randall
Indianapolis Power & Light Co.
P. O. Box 1595B
Indianapolis, IN 46206

Williams, John E.
U.S. Department of Energy
Morgantown Energy Research Center
P. O. Box 880
Collins Ferry Rd.
Morgantown, WV 26505

Wilson, Garry
Sala Allis Chalmers Co.
1913 Terrace Dr.
Sandy, UT 84092

Wong, Monet
Fluor Engineers & Constructors, Inc.
2801 Kelvin
Santa Ana, CA 92714

Wuchter, James
Badische Corporation
602 Copper Rd.
Freeport, TX 77541

Ziegenhorn, George J.
Arco Petroleum Products Co.
400 East Sibley Blvd.
Harvey, IL 60426

Zmuda, Jan T.
Research-Cottrell
P. O. Box 1500
Somerville, NJ 08876